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AIR FORCE CAMBRIDGE RESEARCH LABORATORIES, OFFICE OF AEROSPACE RESEARCH, UNITED STATES AIR FORCE

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Abstract

This report is an effort to collect under one cover the existing theory of three continuous zone refining systems; the zone-void system, the zone-transport system and the matter transport system. The steady-state equations which describe these systems are derived using consistent terminology and under boundary conditions which account for the density change due to melting. The newly developed nondimensional steady-state equations are also derived and the results of an extensive computer study based on these equations are presented in graphical form.

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1. INTRODUCTION

That trace impurities are capable of influencing the physical and chemical properties of their host material has been known for many years. Recently in fact, instances have been found in which trace impurities are responsible for or control critical properties of the matrix material. One of the most dramatic examples of the ability of trace impurities to control a property of its matrix is found in the field of semiconductors. The variation of the type, quantity or distribution of impurities in the part per million to the part per billion range can completely change the electrical properties of a semiconductor. For this reason the control of trace impurities in semiconductors is of primary importance.

In order to systematically study the effect of various impurities and combinations of impurities on the electrical properties of a semiconductor, it became necessary to prepare semiconducting materials which were pure to the part per billion range or better. In the early days of the semiconductor industry the most important semiconductor was germanium. Known purification techniques failed to purify germanium to the required purity level. Pure germanium was finally prepared by a new purification technique developed primarily to purify semiconductor materials. This technique, which was originated by W. G. Pfann, is called zone melting. When materials are purified by zone melting techniques the process is termed zone refining.

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Zone refining is not a technique which resulted from the discovery of new principles. In retrospect one can clearly see that zone refining was a logical extension of the use of the freezing or crystallization process as a means of purification. To use crystallization as a means of purification one takes advantage of a well known physical fact, namely, when a solution starts to freeze the solute is almost always unevenly distributed between the liquid and solid phases. A typical example of this uneven distribution of solute is found in the use of the freezing process to remove salt from sea water. When the temperature of a saline solution is lowered below the freezing point the first ice particles which freeze out have a lower concentration of salt than the original solution. A process based on this fact is being given serious consideration as a means of the large scale preparation of fresh water from sea water in Israel.

Under equilibrium conditions the measure of the inequality of the solute distribution between the solid and liquid phase of such a system is given by the equilibrium distribution coefficient, k_o, which is the ratio of the concentration of solute in the solid C_S to the solute concentration in the liquid C_L. Thus

$$k_o = \frac{C_S}{C_L} \tag{1}$$

The freezing process has been known as a purification technique for a great many years. Its utilization however has been very limited due to the fact that it is an extremely tedious technique to employ. Prior to zone refining the only basic improvements made in art of purification by freezing was fractional crystallization and fractional crystallization was simply a repetition of the freezing process. In fractional crystallization just as in a regular crystallization all of a solution consisting of two or more components is made molten. The solution is then allowed to cool until a predetermined fraction of the total solution has solidified. The solidified fraction is then separated from the melt by mechanical means. In a simple crystallization (assuming a favorable k_o and an ideal binary mixture) the partial separation of the two components obtained in this manner constitutes the entire purification procedure. In a fractional crystallization this process would be repeated using the separated solidified fraction of the first crystallization as the starting solution of the second crystallization. The number of crystallizations used would depend on the purity of the product desired. Probably the most famous application of fractional crystallization was the separation of radium from barium by the Curies. The fact that by use of this technique the Curies and others were able to effect the remarkable separations they did is a tribute to their analytical technique and their determination rather than the efficiency of the technique.

Purity via fractional crystallization is an arduous, tedious chore. This process requires that the material being purified undergo a change in state. The drawback of the process is that one of these states is the solid state. The reason that the solid state poses such difficulties in a purification process is that under normal conditions solids do not flow. When the solid state is met in such a process, the separation of pure and impure fractions must be effected by the operator and not by the materials themselves (as is the case in distillation). Unfortunately, until zone refining was discovered fractional crystallization was the only purification method employing the freezing principle, by which a separation factor of any given multiple of the distribution coefficient could be obtained.

The production of single crystals from the melt is an application of the freezing process. Therefore under ideal conditions for crystal growth, the measure of the distribution of impurities between the solid and the liquid at the freezing interface is given by the distribution coefficient. In the Bridgeman[1] process for crystal growth, where both the melt and the growing crystal are contained in the same crucible and solidification proceeds slowly from one end; if the distribution coefficient, k, is less than one, the growing crystal injects impurities into the liquid. When crystallization is complete the impurities will be unevenly distributed throughout the crystal.

Making the following assumptions:

1. The original solution is an ideal binary mixture
2. Diffusion in the solid is negligible
3. Uniform solute distribution in the liquid
4. k (the effective distribution coefficient of the growing crystal) is constant

Pfann[2] reports that C, the concentration of impurity at any plane along the crystal, can be expressed by Eq. (2). Thus,

$$C = kC_o(1-g)^{k-1} \tag{2}$$

where

C = solute concentration in the solid at the liquid-solid interface, in units of solute per unit volume of solution.

C_o = initial impurity concentration

and

g = the fraction of the original solution that has solidified.

Pfann[2] called this type of freezing process <u>normal freezing</u>. Equation (2) of course assumes a crystal or ingot of uniform cross section whereas in the Bridgeman technique the ingot usually tapers to a point at one end.

In 1952, Pfann[2] reported the basic principles of zone melting. Zone melting is a technique whereby the freezing process could be carried out on an ingot in such a way that impurities could be distributed in a manner which differed from that which would be produced by a normal freeze. The main difference between zone melting, fractional crystallization and normal freezing is in the amount of material that is made molten at any one time. In both fractional crystallization and normal freezing all of the material undergoing treatment is made molten at the start of the process. For zone melting only a fraction of the total material is made molten at any one time. Zone melting is normally accomplished, as shown in Figure 1, by arranging the material to be treated in the shape of a bar and causing a molten zone to travel from one end to the other. The solute distribution which results from the passage of such molten zones along a bar is a function of many parameters among which are: the distribution coefficient, the original solute distribution, the number of zones which traverse the bar, the direction in which these zones travel, the size of the zones and the length of the bar. It is obvious that a great many different solute distributions are possible. The methods for controlling these solute distributions by variation of these parameters are called zone melting techniques.

The most important application of zone melting is in the purification of materials. Zone melting techniques which are designed specifically to purify materials are called zone refining techniques. For simplicity the discussions of zone refining which follow will be restricted to the purification of an ideal binary solution in which the solute (impurity) is present in very low concentrations and k is constant. In this system we also assume that there is no diffusion in the solid and complete diffusion in the liquid. These assumptions which will hold for the remainder of this report are very closely approximated in most zone refining systems.

The equilibrium distribution coefficient k_o can be determined from the phase diagram of the binary system being purified. If the solute raises the melting point of the solvent then $k_o > 1$; however, if the solute lowers the melting point of the solvent then $k_o < 1$. The value of k_o can be attained only under perfect equilibrium conditions. In an actual zone refining operation the value of k_o can only be approached. The value of the effective distribution coefficient, k, the distribution coefficient which actually exists, can and must be determined experimentally for any given system. If normal experimental care is exercised the assumption of a constant k for dilute solutions is quite reasonable.

Purification via zone refining is accomplished by passing a number of molten zones through an ingot of the material to be purified. All the zones travel in the same direction. The number of zones is predetermined by the purity desired. The direction of travel of impurities is a function of the effective distribution coefficient. For $k < 1$, impurities collect in the liquid and travel with the zones.

For $k > 1$, impurities are rejected into the solid and travel in the direction opposite to the zones travel. The degree of purification is a function of the number of zones passed through the ingot and approaches a limit as the number of zones used approaches infinity.

The equation which describes the solute distribution in an ingot after one molten zone (pass) has been put through the ingot was reported by Pfann.[2] This equation Pfann expressed as:

$$\frac{C}{C_o} = 1 - (1-k)\, e^{-\frac{kx}{\ell}} \tag{3}$$

Equation (3) describes the solute distribution which exists in all but the last zone length of the ingot. A complete derivation of Eq. (3), the idealizing assumptions on which it is based, and the definitions of the terms involved are given in Appendix A. An equation describing the solute distribution in an ingot following the passage of more than one molten zone is not easily derived. Lord[3] and Reiss[4] were the first to present approximate solutions. It was left to Braun and Marshall[5] to generate a complete analytical solution for multipass solute distributions. Even with Braun's expressions, however, obtaining the solute distribution which exists after five or more passes requires a great deal of computation and is a problem which is more realistically solved by a computer.

The separation of impurities obtainable by passing molten zones through a charge increases as the number of passes increases until a steady-state or ultimate distribution is reached. When the steady-state is obtained, the passage of additional zones through the ingot does not alter the solute distribution. The equations which describe this distribution were first presented by Pfann.[2] They are:

$$C(x) = A e^{Bx} \tag{4}$$

where

$$k = \frac{B\ell}{e^{B\ell} - 1} \tag{5}$$

and

$$A = \frac{C_o BL}{e^{BL} - 1} \tag{6}$$

A derivation of these equations is given in Appendix B. These equations do not take into account the back reflection of solute due to the effect of the normal freeze in the terminal zone of the charge. Braun[6] presents a solution for the ultimate distribution, for any value of k, which takes into account the effect on the ultimate distribution due to the normal freeze which occurs in the final zone during each pass.

Zone refining is an easy way to carry out a fractional crystallization. The simple change in procedure namely, the passage of molten zones has greatly increased the efficiency of crystallization as a purification technique in that it has automated the separation of pure and impure fractions. A number of molten zones can be passed through an ingot in a single operation providing, in simple fashion, the end of fractional crystallization which, as has already been mentioned, is a separation factor which is any given multiple of the distribution coefficient.

2. CONTINUOUS ZONE REFINING

Zone refining as described by Pfann in Reference 2 is a multistage batch process. Such a batch process can in many instances fulfill all of the requirements involved in the production of a pure material. Batch processes, however, have many intrinsic limitations which can be eliminated if the process can be made continuous. In general, a continuous purification process is one which comprises an enriching and a stripping section and the means for the introduction of feed and the removal of product and waste. The addition of feed to a continuous system must occur at a point in the system which is between the places where product and waste are removed. Continuous fractional distillation is the analog of continuous zone refining which treats the phase change between vapor and liquid. In principle they are very similar. In practice the ability of the vapor phase to be compressed easily and the fact that the liquid phase flows and does not build up on the container walls allows the feed to be introduced easily at any point on a distillation column and also provides counter current flow. In a zone refining system things are not quite so simple. Here neither phase is easily compressed and the solid instead of flowing freely usually adheres tenaciously to and builds up on the container walls. The continuous zone refiner must live with these difficulties and still provide for the requisite flows of feed, product and waste while permitting the unidirectional movement of molten zones down the column. Such a system is shown in generalized form in Figure 2.

The creation of molten zones and the mechanism by which these zones are made to traverse the column are experimental problems and therefore are beyond the scope of this paper. It will be assumed that the mechanism for their creation

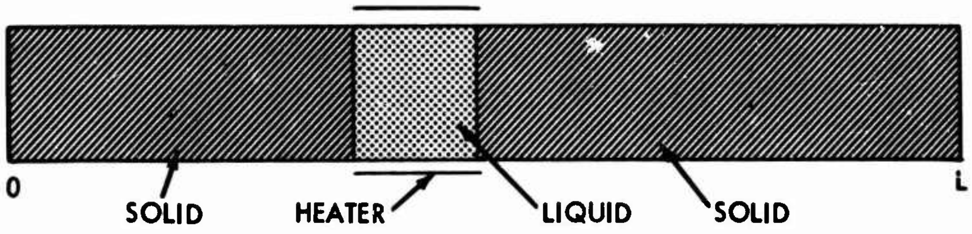

Figure 1. A Molten Zone Being Passed Through an Ingot of Length L

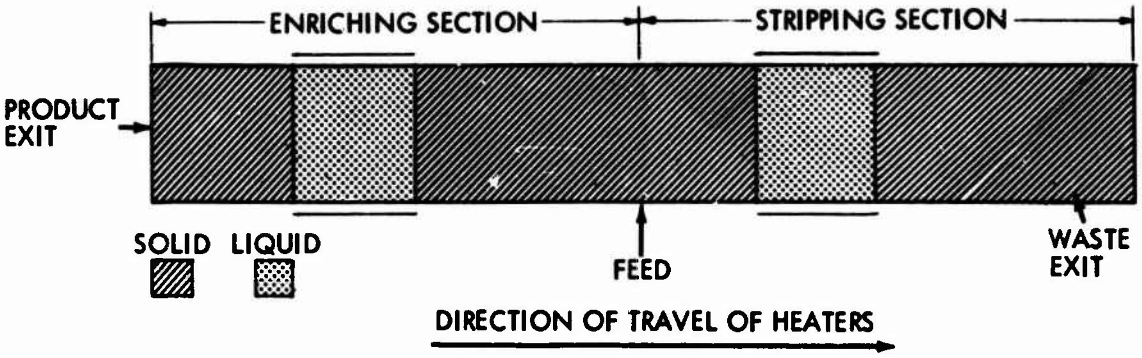

Figure 2. A General Continuous Zone Refining Apparatus

and movement has been found and that this mechanism produces zones which have planar interfaces, are of constant size and move at a rate of travel which is constant.

In 1955, Pfann[7] described the zone-void system, the first zone refining system postulated capable of completely continuous operation. In this system the movement of material into and out of a system is brought about by the movement of voids inside of the system. Voids are normally gas filled spaces, however, in a more general fashion Pfann[8] has defined a void as a region in which there is a substantial deficiency of the material undergoing treatment. Material movement is produced by causing voids formed at the product and waste exits to move to the feed inlet. The column is constructed in two parallel vertical sections joined together at the top by the feed section. An example of this type of apparatus is shown in Figure 3. Voids are created at the bottom of each section by the controlled removal of a small amount of material from the column. The size of the void must be less than one molten zone. Several methods of forming voids have been reported.[8,9] Product and waste are collected at the bottom of the enriching and stripping sections, respectively, in forming the voids. Material is moved down the column as a result of movement of the molten zones which cause the voids to move upward. When the voids reach the top of the section they are filled in by feed. Thus, feed is introduced into a column every time a void reaches the feed section. In the enriching section, voids travel continuously with the molten zones while in the stripping section their travel is intermittent, a zone length at a time.

One of the primary advantages of continuous operation is the ability to operate at or near the steady state. The time required to attain this distribution will vary from system to system, however, even if the start up time is long, once attained, the system continues to deliver material of maximum purity.

Pfann[7] has shown that for any continuous zone refining system the overall material balance in terms of the volume flow rates of feed, F, waste, W, and product, P, is given by:

$$F = W + P \tag{7}$$

In a continuous zone refining system it is the function of the enriching section to produce a pure product. In doing this the enriching section injects into the feed the impurities which it has removed from the product it produces. Without a stripping section this injection of impurities into the feed would eventually increase the solute concentration in the feed to the point where no purification would be obtained. The function of the stripping section is to inject into the feed material of sufficient purity and in sufficient quantity to maintain the solute concentration in the feed constant. When the stripping section accomplishes this function the solute balance for the system is given by

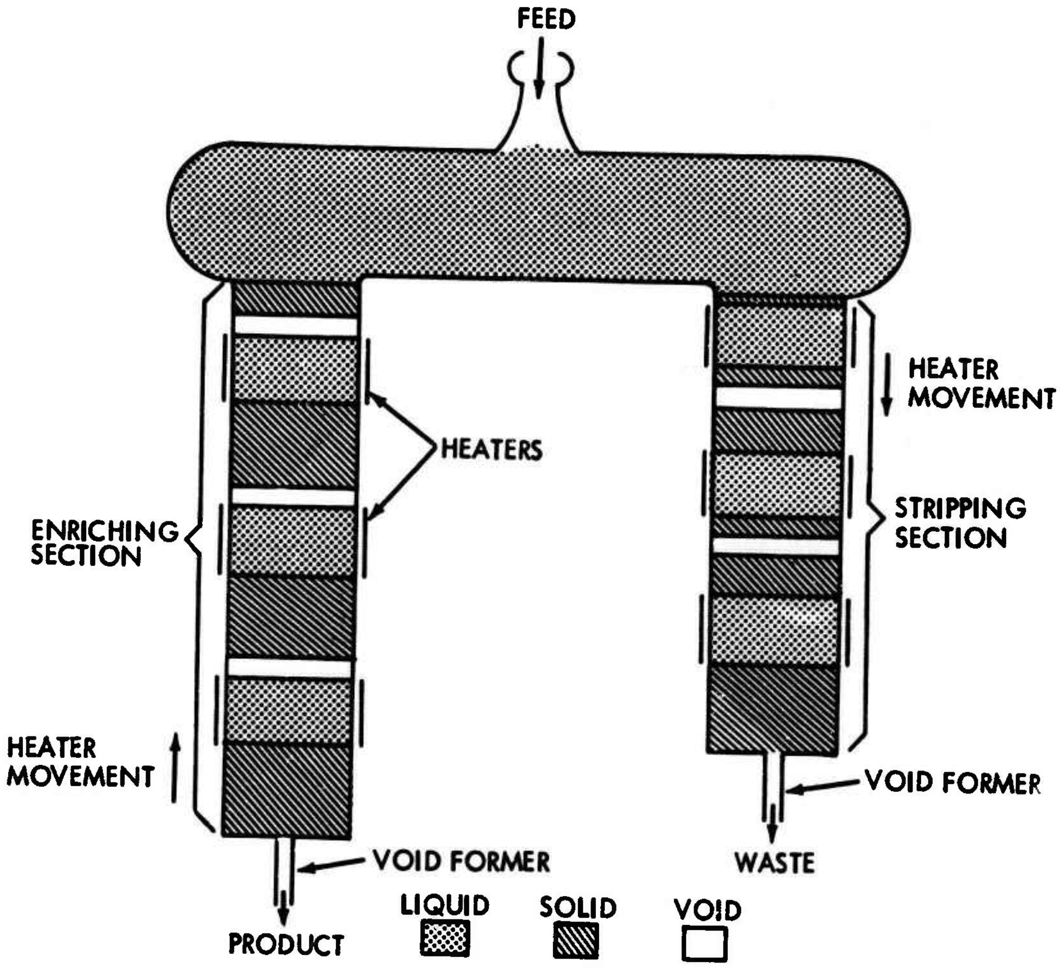

Figure 3. A Zone-Void System

$$FC_f = PC_p + WC_w \tag{8}$$

where C_f, C_p, and C_w are the solute concentrations in, respectively, the feed, product, and waste. When

$$C_p = \alpha C_f \tag{9}$$

and

$$C_w = \beta C_f \tag{10}$$

the ratio of the flows of product to waste (P/W), which will provide this solute balance can be found by substituting Eqs. (7), (9) and (10) into Eq. (8). Thus

$$\frac{P}{W} = \frac{\beta - 1}{1 - \alpha} \tag{11}$$

Purity requirements and the solute concentration in the feed determine α. When the steady state has been reached the weight of solid material, L_e, that must be in the enriching section to effect the constant removal of a product of concentration C_p can be obtained by solving the steady-state equations. Thus, for a material of known k, in a system using a molten zone of convenient weight, ℓ, and a convenient void size, L_e is given by

$$L_e = \frac{1}{0.434\, B_e} \log\left[\omega\left(\frac{\psi}{\alpha} - 1\right)\right] \tag{12}$$

where B_e, ω and ψ are constants which depend on h, ℓ and k and are given by:

$$e^{B_e h} = 1 + \frac{B_e \ell}{k} \tag{13}$$

$$\omega = \frac{k}{(1-k)\, B_e \ell}\left[1 - e^{B_e (h-\ell)}\right] \tag{14}$$

$$\psi = \frac{hk - \ell}{h - \ell} \tag{15}$$

The derivation of Eqs. (13) to (15) was first reported by Pfann.[7] The authors have modified the definitions of terms originally used by Pfann to account for the change in density due to melting. The derivation of Eqs. (13) to (15) along with the definitions of previously undefined terms is given in Appendix C.

The steady-state solute distribution these equations describe is shown in Figure 4. The mathematical model does not give any information about the actual total weight of material in the enriching section, however, Pfann[7] reports that in practice this weight is usually equal to $L_e + h$.

Pfann[7] also presented the steady-state equations for the stripping section of the zone-void system. As a result of his derivation Pfann reported that in the stripping section the length of column L_s which will produce a separation β is given by

$$L_s = \frac{1}{0.434\,B_s} \log\left[\left(\frac{\beta\delta - k}{\gamma}\right) + 1\right] \qquad (16)$$

where B_s, δ and γ are constants and functions of h, ℓ, k and β which can be obtained by the following:

$$e^{B_s \ell} = 1 + B_s \frac{h}{k} \qquad (17)$$

$$\delta = k\left(\frac{h-\ell}{h}\right)^{1-k} \qquad (18)$$

$$\gamma = \frac{B_s\left[(h-\ell)\,\beta - h\,(1-k)\right]}{1 + B_s h - e^{B_s h}} \qquad (19)$$

As part of the theoretical continuation of the zone refining effort in this laboratory a study of the effect of variation of the significant parameters of the zone-void system was undertaken. The parameters under study were h, ℓ, and k (as defined by Pfann[7]). The object of this study was to determine the effect of these parameters on α and β.

In the stripping section the definition of k and β precludes the possibility of β assuming values less than unity when $k < 1$. In the course of this investigation it was found that computations based on Eqs. (16) to (19) gave values of β less than unity in the region $1 > k > \ell/h$ for almost all values of L_s. Further computations showed that β assumes negative values when $k > 1$ for many values of L_s, ℓ and h. A study of Pfann's derivation of Eqs. (16) to (19) revealed an error in the equation describing the solute balance over the entire cycle.

(Equation (28), Reference 7.) This error invalidated the final equations of Pfann's derivation.

The equation of the correct solute balance is

$$h\, C_f = \int_0^{\ell} C(x)\, dx + (h-\ell)\,\beta\, C_f \tag{20}$$

Using Eq. (20), corrected steady-state equations which account for the change in density due to melting are derived as shown in Appendix D. In this derivation terms are redefined to account for the density change. Based on these corrections and the accompanying definition changes L_s is given by

$$L_s = \frac{1}{0.434\, B_s} \log\left[\frac{\beta\,(\delta-k\mu)}{k\,(1-\beta\mu)}\right] \tag{21}$$

where

$$e^{B_s(\ell-w)} = 1 + B_s \frac{\ell}{k} \tag{22}$$

$$\delta = k\left(\frac{w}{\ell}\right)^{1-k} \tag{23}$$

and

$$\mu = \frac{w}{\ell - k\,(\ell-w)} \tag{24}$$

Calculations based on Eqs. (21) to (24) remove the aforementioned inconsistencies in β. Figure 5 shows the steady-state solute distribution in the stripping section. A paper describing part of this phase of the effort has been published elsewhere.[10]

After the error in Eq. (28) of Reference 7 and its implications with respect to the zone-void system had been noted (as above), Pfann[11] pointed out that Abe[12] using an independent method had derived steady-state equations for the zone-transport system and had already reported the existance of this error in a paper which treated the zone-transport system. The zone-transport system, a continuous zone refining system, was also invented by Pfann.[13, 14] An example of a zone-transport apparatus is shown in Figure 6. In this system movement of material from the feed section to the product and waste exits is accomplished by virtue of the difference in level between the feed and the product and waste exits. Because

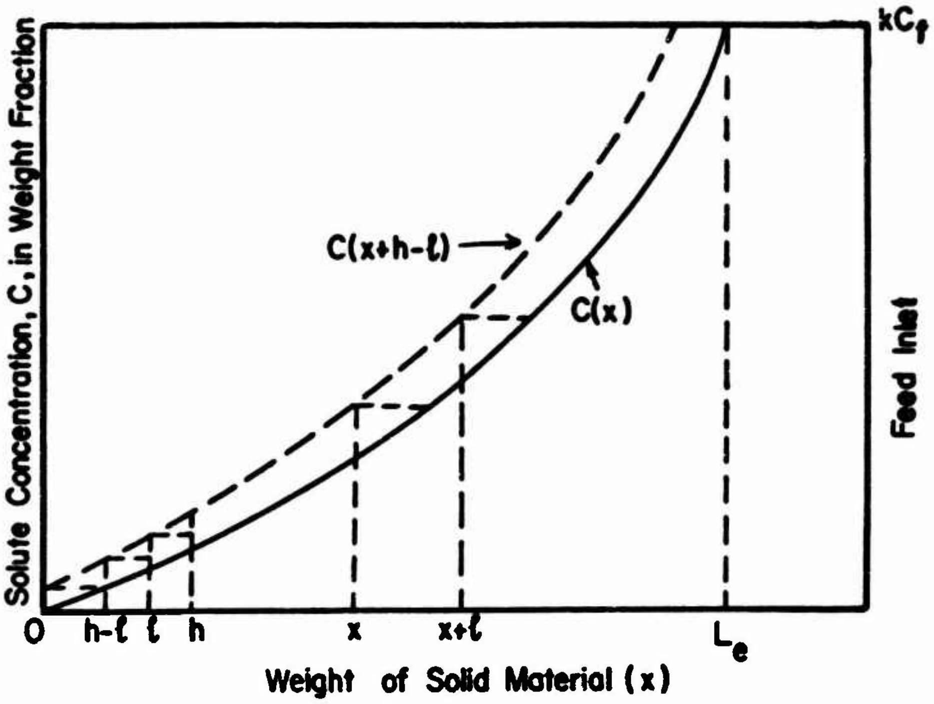

Figure 4. Steady-State Solute Distribution in the Enriching Section of the Zone-Void System

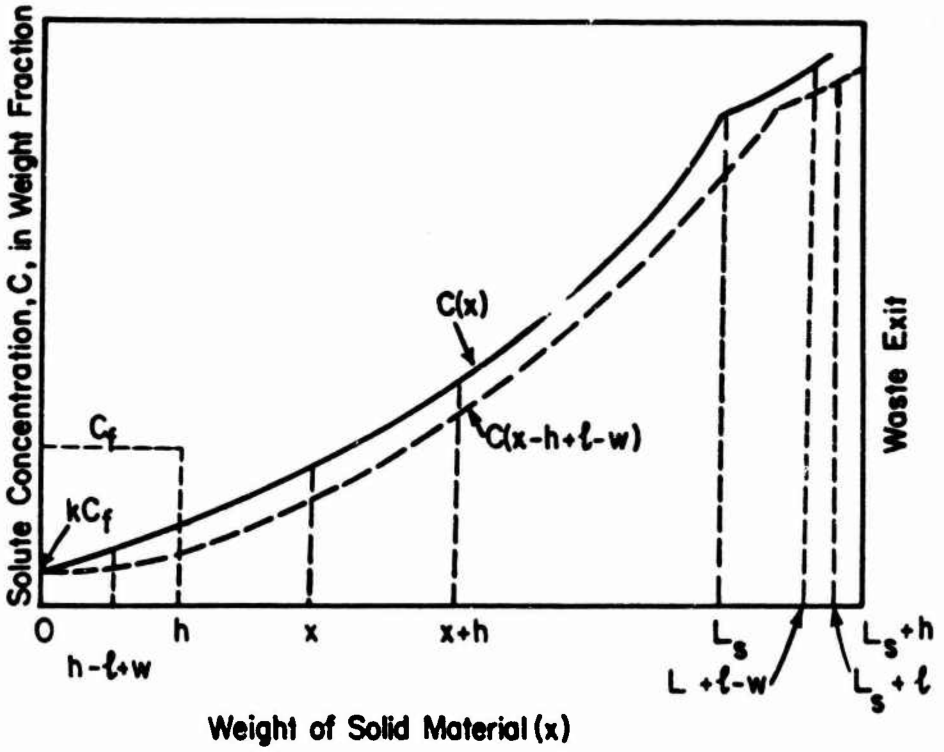

Figure 5. Steady-State Solute Distribution in the Stripping Section of the Zone-Void System when the Terminal Zone Undergoes a Normal Freeze

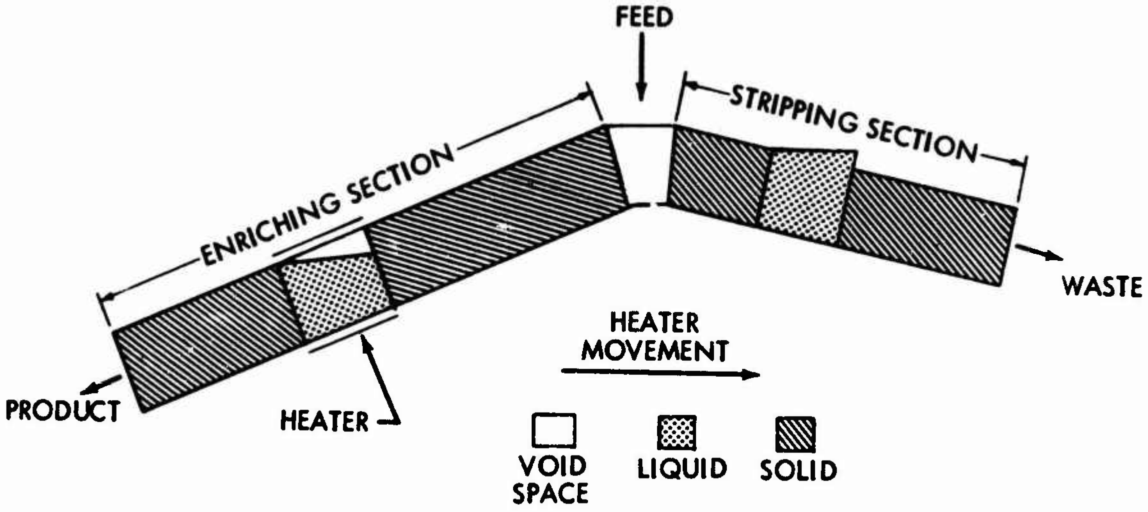

Figure 6. A Zone-Transport System

of this difference in level, material in the molten zones flows down hill. The weights of material produced, per pass, at the product and waste exits respectively were given by Pfann[14] as

$$P = \frac{h_a \ell^2}{2 L_e} \tag{25}$$

$$w = \frac{h_b \ell^2}{2 L_s} \tag{26}$$

In describing conditions existing when the steady state has been obtained, Pfann[14] stated that the steady-state equations which describe the zone-void system could be used to describe the zone-transport system provided the same assumptions are made and that the expressions for the parameters which define material flow were changed in accord with Table 1. Our investigation has shown that this is not a valid transition due to the fact that the solute concentrations in the product and waste which are used as parameters in the derivation of the steady-state equations are different in the zone-void and in the zone-transport systems. Thus in the zone-void system C_p is given by Eq. (27) and C_w by Eq. (28).

TABLE 1. Expressions for the material flow parameters in each system when constant density is assumed

	Pfann Zone-Void	Pfann Zone-Transport	Abe Zone-Transport
Enriching Section	$h - \ell$	P	P
	ℓ	ℓ	$\ell - P$
	h	$P + \ell$	ℓ
Stripping Section	$h - \ell$	W	W
	h	ℓ	$\ell + W$
	ℓ	$\ell - W$	ℓ

Thus

$$C_p = \frac{1}{h - \ell} \int_0^{h-\ell} C(x)\, dx \tag{27}$$

The value of C_w depends upon the mode of freezing in the last zone. In the zone-void system C_w is defined as the average solute concentration of the charge between $L_s + \ell$ and $L_s + h$.

Thus

$$C_w = \frac{1}{h - \ell} \int_{L_s+\ell}^{L_s+h} C(x)\, dx \tag{28}$$

In the zone-transport system, because of the physical difference in the mode of collection of the product and the waste, C_p is given by Eq. (29).

$$C_p = \frac{1}{h} \int_{o}^{h} C(x)\, dx \tag{29}$$

while

$$C_w = \frac{C(L_s)}{k} \tag{30}$$

In his study of the zone-transport system Abe[12] transformed Pfann's zone-void steady-state equations into Pfann's zone-transport equations by following Pfann's directions.[14] Using Pfann's zone-transport steady-state equations Abe made calculations which revealed the same inconsistencies in β noted previously.

Using his own technique Abe[12] derived steady-state equations for the zone-transport system. These derivations are given in Appendices E and F. Using his own equations Abe[12] found that all of the inconsistencies in α and β were eliminated.

In his paper Abe[12] compared the limits of α and β obtained when his zone-transport equations and Pfann's zone-transport equations were used (at constant density). This comparison revealed three main discrepancies. These discrepancies are:

1. In the enriching section when $k \neq 1$ and $L_e = 0$, Pfann reports $\alpha = \omega\psi/1 + \omega$ whereas Abe finds $\alpha = 1$ when $L_e = 0$ irrespective of the value of k. Where in the zone transport system, ω, ψ, L_e, ℓ and P are defined by Pfann[14] as follows:

$$\omega = \frac{k}{1 - k B_e \ell} \left(1 - e^{B_e P}\right)$$

$\psi' = k + \frac{(k-1)\ell}{P}$

L_e = the distance from the exit end of the enriching section to the plane at which the solute conc. in the solid is kC_f

ℓ = the length of the molten zone

P = the volume of product collected per pass

2. In the stripping section when the actual length of the stripping section minus one zone length (Pfann calls this length L_s, Abe calls it L'_s) equals infinity and $k = 1$, Pfann's equations show $\beta = 0$ whereas Abe's equations yield $\beta = 1$.

3. In the stripping section when the distance defined as the actual length of the stripping section minus one zone length is large enough and when $k > 1$, Pfann's equations yield $\beta < 0$ whereas under the same conditions, Abe's equations have $\beta = 0$ when $k > (\ell+w)/\ell$ (where ℓ and w are defined by Abe).[12]

The authors have pointed out[15] that in their opinion these differences and other differences, which become apparent when References 7 and 12-14 are studied carefully, are the result of three factors:

1. Partially inconsistent definition of terms.
2. The error in Eq. (28) of Reference 7.
3. The transformation of the steady-state equations of the zone-void system to the steady-state equations of the zone-transport system without taking into account the difference in the mathematical expressions of the product and waste concentrations in each system.

The derivation of the steady-state equations for the zone-transport system as reported by Pfann[14] and Abe[12] are different and are based on different assumptions. However, in the enriching section of each system a comparison of the expressions that define material flows is straightforward since the physical and mathematical significance of these flows is identical. For the stripping section a comparison of the expressions that define material flows is complicated by the different methods of derivation. Thus, in the stripping section, the physical volume of the zone that is maintained molten and caused to travel by a moving heater is, for the purpose of each derivation, different. The mathematical significance of the molten zone in each derivation, however, is identical. Table 1 lists the expressions for the parameters that define the same material flows in Pfann's zone-void system as well as Pfann's and Abe's zone-transport systems. The differences in definition of terms between systems which Table 1 clearly shows are not explicit in Abe's[12] paper.

The definitions of terms used to define column lengths are also partially inconsistent or different. For the zone-void system (and hence the zone-transport system) Pfann[14] defines L_e as the distance from the exit end of the enriching section to the plane at which the solute concentration in the solid is kC_f and comments that in practice this length will usually be one heater length less than the actual section length. For the zone-transport system, Pfann[14] defines the actual length of the enriching section as L_E. In Reference 12, Appendix B, Abe defines L_e the same way Pfann does; however, in Appendix A and Figures 1a and 2 of Reference 12, L_e is shown as the actual section length.

In the stripping section of the zone-void system, Pfann[14] defines the length L_s by

$$L_s = L_s' - h - n_v(h-\ell)$$

where L_s' is the actual length of the stripping section and n_v is the number of void encounters. Since there are no voids in the zone-transport system, Pfann's definition of L_s for the zone-transport system is given by

$$L_s = L_s' - h$$

Abe on the other hand defines L_s as the actual which is the reverse of Pfann's terminology. Thus for Abe

$$L_s' = L_s - h$$

The authors can find nothing wrong with the definition of terms used by Pfann to describe his zone-void or zone-transport systems. Therefore since Pfann invented both systems and because of the almost universal acceptance of his terminology except where difficulties were encountered in treating the density change due to melting, the authors have tried to adhere rigidly to his terms and definitions of terms.

This is true even in Appendices E and F where we use Abe's derivation of the steady-state equations.

In his derivation of the steady-state equations for the zone-transport system Abe introduces the term γ, ρ_s/ρ_ℓ, to account for the density change due to melting. The authors feel that a simpler method of accounting for this density change in all continuous zone-refining systems is to redefine terms by expressing solute concentration in weight-fraction as suggested by Pfann[16] and to change the units of measure of position along a column from length to weight of solid material.[15] When these changes are made the expressions for the material flow parameters and their respective definitions for each system are given in Table 2.

Abe's derivation of the steady-state equations for the zone-transport system as given in Appendices E and F have been modified in light of these decisions concerning the definition and consistency of terms and the handling of the density

TABLE 2. Expressions for the material flow parameters in each system when the density change due to melting is taken into account

	Pfann Zone-Void	Pfann Zone-Transport	Abe Zone-Transport	Definition
Enriching Section	$h - \ell$	P	P	Weight of product collected per pass
	ℓ	ℓ	$\ell - P$	Weight of liquid material in the molten zone that is maintained molten and caused to travel by a moving heater
	h	$P + \ell$	ℓ	Weight of material equal to the weight of liquid material that is maintained molten and caused to travel by a moving heater plus the weight of product collected per pass
Stripping Section	W	W	W	Weight of waste collected per pass
	ℓ	ℓ	$\ell + w$	Weight of liquid material in the molten zone that is maintained molten and caused to travel by a moving heater
	h	h	ℓ	Weight of solid material that would fill the volume occupied by the molten zone when the cross section of the column is unity.*

*In Abe's zone-transport system this volume is smaller than the volume of the molten zone.

change due to melting. These changes correct an error in the handling of density present in Abe's derivation of the steady-state equations in the stripping section.[15]

A derivation of the steady-state equations for the enriching section of the zone-transport system is given in Appendix G. This is the same derivation outlined by Pfann[14] except that it has been modified in light of Table 2 and to account for the different product concentrations which exist in the zone-void and the zone-transport systems. As a result of this modification, the expression for L_e is given by:

$$L_e = \frac{1}{0.434\ B_e} \log \left[\frac{\omega k (P+\ell) + \ell}{\alpha (P+\ell)} - \omega \right] \tag{31}$$

where

$$\omega = - \frac{P}{(P+\ell)(1-k)} \tag{32}$$

and

$$e^{B_e(P+\ell)} = 1 + \frac{B_e \ell}{k} \tag{33}$$

In the stripping sections of both the zone-void and zone-transport systems the shift in the solute distribution due to the mode of freezing of the final zone at the end of each pass has not been treated analytically. Therefore due to the fact that the waste is withdrawn from the zone-transport system before the last zone begins to freeze the solute concentration in the waste (back reflection not considered) is independent of the mode of freezing in the terminal zone. The steady-state equations for the stripping section of the zone-transport system can be derived as shown in Appendix H. This is the same derivation used by Pfann to describe the stripping section of the zone-void system corrected for the error in Eq. (28) of Reference 7 and using the proper waste concentration (Eq. (30)). Using this derivation L_s is given by

$$L_s = \frac{1}{0.434\, B_s} \log \left[\frac{\beta(1-\mu)}{1-\beta\mu}\right] \tag{34}$$

where

$$e^{B_s(\ell-w)} = 1 + \frac{B_s \ell}{k} \tag{35}$$

and

$$\mu = \frac{w}{k(w-\ell)+\ell} \tag{36}$$

Abe's derivation of the zone-transport equations (Appendices E and F) differs substantially from Pfann's corrected derivation (Appendices G and H). However, both derivations describe the same system and unless the mathematical model is different the expressions for L_e which result should be identical. Algebraic manipulation using Table 2 shows that this is, indeed, the case.

The limits of α and β therefore are also identical. These limits and those for the zone void system are shown in Table 3.

TABLE 3a. Limits of α and β for the zone-transport system

Range of α

	Value of k	$L_e = 0$	$L_e = \infty$	Sign of B_e
Enriching Section	$k \leq \frac{\ell}{P + \ell}$	1	0	+
	$k \geq \frac{\ell}{P + \ell}$	1	$\frac{kP + \ell(k-1)}{P}$	-

Range of β

	Value of k	$L_s = 0$	$L_s = \infty$	Sign of B_s	Sign of μ
Stripping Section	$k \leq \frac{\ell}{\ell - W}$	1	$\frac{kW + \ell(1-k)}{W}$	+	+
	$k \geq \frac{\ell}{\ell - W}$	1	0	-	-

b. Limits of α and β for the zone-void system

Range of α

	Value of k	$L_e = 0$	$L_e = \infty$	Sign of B_e
Enriching Section	$k \leq \frac{\ell}{h}$	$\frac{w\psi}{1 + w}$	0	+
	$k \geq \frac{\ell}{h}$	$\frac{w\psi}{1 + w}$	ψ	-

Range of β

	Value of k	$L_e = 0$	$L_e = \infty$	Sign of B_s	Sign of μ
Stripping Section	$k \leq \frac{\ell}{\ell - w}$	$\frac{k}{\delta}$	$\frac{kW + \ell(1-k)}{W}$	+	+
	$k \geq \frac{\ell}{\ell - w}$	$\frac{k}{\delta}$	0	-	-

Table 3, Table 2, and algebraic manipulation, where required, reveals that the limits of α and β are the same for the zone-void and the zone-transport system when L_e and L_s are infinite. When $L_s = 0$ the value of β in the zone-void system is k/δ while in the zone-transport system $\beta = 1$. In the stripping section of both systems when $L_s = 0$ the actual weight of material in the section is ℓ. The difference in the value of β when $L_s = 0$ is due to the difference in the method of waste collection. In the zone-transport system the waste is collected when the last zone is completely molten. The solute concentration in the waste then is equal to feed concentration when $L_s = 0$ and therefore α must equal unity. In the zone-void system the waste is not collected until a weight of material $\ell - w$ of the last zone has frozen then the remaining liquid, w, is collected as waste. When $L_s = 0$ the whole column is the last zone and the last zone is assumed to freeze by a normal freeze. It is easily shown that under these conditions β must equal k/δ.

When $L_e = 0$, $\alpha = \omega\psi/1+\omega$ in the zone-void system while in the zone-transport system $\alpha = 1$. This difference in the limit of α is due to the different mechanisms of product collection and the change which these mechanisms make on the mathematical definition of the solute concentration in the product. Within the limits of the mathematical models both limiting values of α are correct.[15]

The first zone-void system to demonstrate Pfann's hypothesis was built at this laboratory for the purification of SiI_4.[17] Buford and Starks[18] later continued this effort for this laboratory on a contractual basis. In an effort to eliminate some of the experimental deterrents to ultrapurification inherent in the zone-void system Moates et al[19] designed a new continuous zone refining system. A complete description of this system has been presented elsewhere.[20] This system which we refer to as the matter transport system uses the matter transport phenomenon described by Pfann[21,14] as the driving force for material flow in either the enriching or stripping section of the system. Material movement in the other section is accomplished by means of voids.

In his description of the zone-void system Pfann always considered $\rho_s = \rho_\ell$. In the zone-void system if the change in density which occurs in going from the solid to the liquid state (or vice versa) is taken into account, material can be made to flow even if the voids are reduced to zero volume in one of the arms. In such an arm, material flow is accomplished by collecting an amount of material per pass that is equal to the difference in volume between a zone of material in the cold and hot condition. Figures 7 and 8 show two systems which utilize this principle.

In order to simplify the description of the operation of these systems, assume $\rho_s > \rho_\ell$ and $k < 1$. Then in Figure 7 the enriching section is on top, the heaters travel downward and matter transport moves material from the mid-feed upward to the product exit. At the start of each cycle the uppermost heater is in position at the top of the section. It melts the solid starting at the product sidearm down

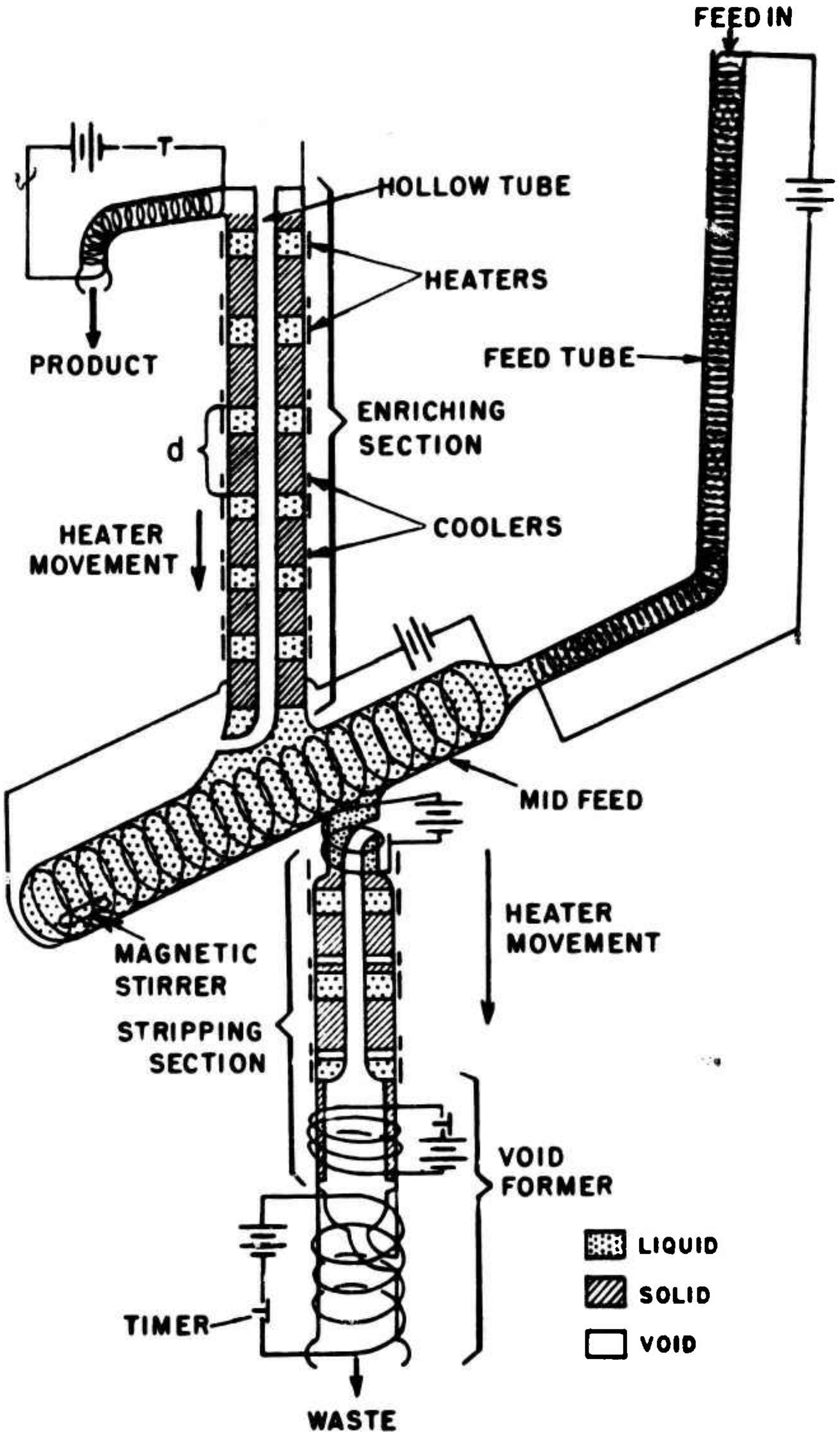

Figure 7. Matter Transport System with Feed Section Located in the Middle

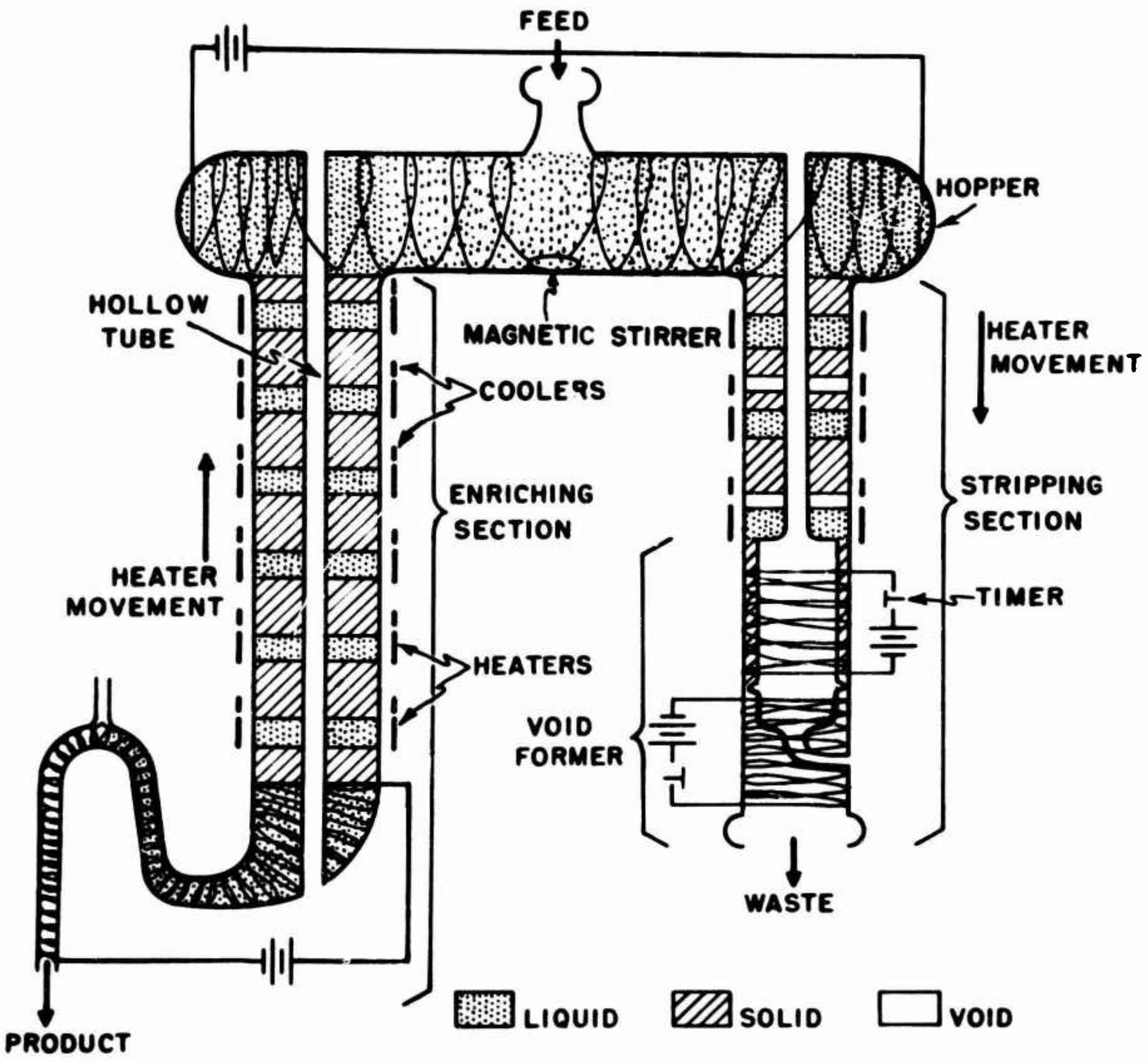

Figure 8. Matter Transport System with Feed Located Above

to a plane where a weight of solid material h has melted. The liquid expands overflowing into the product sidearm and down into the product container. As the heater travels down the column, solid freezes at the level of the sidearm. When the liquid zone reaches the mid-feed, it joins its liquid length with the mid-feed and then reciprocates. The liquid zone that was brought down contracts on freezing, drawing up into the column a volume of feed equal to the volume of product which has been collected in that pass. Repetition of this process (that is, the passage of molten zones) provides both purification by the freezing process and continuous material movement via the matter transport phenomenon.

In Figure 8, the apparatus is arranged in the same manner as a conventional zone-void refiner. The enriching and stripping sections are both below the feed. In the matter transport section, the enriching section, the heaters travel upward. Material movement in this section is downward and product is collected at the bottom. Material movement is produced by the same steps used to describe Figure 7. The only difference is that when the heaters start a pass, the bottom heater melts in a weight of solid material h, as before, however the expanding material instead of overflowing directly, as in Figure 7, pushes the molten material below it down and then up over the inverted U-tube in the product collector.

The stripping sections in both Figures 7 and 8 are identical and use examples of the void-former already described.[9]

A derivation of steady-state equations describing the enriching section of a matter transport system is not as clear-cut as in the zone-void or zone-transport systems. In the zone-void and zone-transport systems experimental product collection provides a concise mathematical definition of the solute concentration existing in the product (Eqs. (27) and (29) respectively). The best description of the solute concentration in the product of a matter transport system is that it lies somewhere between that predicted by the zone-void and the zone-transport equations.[22] The conservative estimate, which the authors prefer, is given by the zone-transport steady-state equations. This derivation has already been given (Appendix G).

The stripping section of the matter transport system uses a void-former and if freezing in the terminal zone is by normal freeze the derivation of the steady-state equations is the same as the zone-void system (Appendix D). If the void-former described in Reference 9 is used, freezing in the final zone of each pass is not accurately described by the normal freeze mechanism. The actual freezing process is somewhere between a normal freeze and a uniform freeze. If the terminal zone freezes by a uniform freeze, the derivation of the steady-state equations would be that given in Appendix H.

The expressions used to define material flow in the matter transport system[20] were those originally used by Pfann[5] defined on a weight basis. To make terminology consistent within this report the expressions used to define the zone-void system, Table 2, can be used to describe the matter transport system noting that in the matter transport stripping section $h - \ell$ is the same as w in Table 2.

For the three continuous zone refining systems described thus far, the zone-void, the zone-transport, and the matter transport systems, only two sets of steady-state equations exist for each section. These equations are, however, relatively complex. An evaluation of the effect of variation of some of the pertinent parameters by the iterative substitution of various values of the parameters in question is a time consuming, arduous task. By nondimensionalizing to obtain the minimum number of parameters it is feasible with the aid of a high speed digital computer, to show, in graphical form, the effect of the variation of any of the physical parameters on the enriching and stripping sections of each system. The nondimensionalization transforms the steady-state equations of each section into a pair of equations we call universal equations. An equivalence table for the nondimensional variables is given in Table 4. The derivation of the universal equations for each section is given in Appendices I-L.

TABLE 4. Nondimensional terminology equivalence

	Pfann Zone-Void System	Pfann Zone-Transport System	Abe Zone-Transport System	Nondimensional Parameters
Enriching Section	$B_e h$	$B_e(P+\ell)$	$B_e(P+\ell)$	v
	$\frac{\ell}{h}$	$\frac{\ell}{P+\ell}$	$\frac{\ell}{P+\ell}$	y
	$\frac{L_e}{h}$	$\frac{L_e}{P+\ell}$	$\frac{L_e}{P+\ell}$	z
Stripping Section	$B_s\ell$	$B_s\ell$	$B_s(h+w)$	v
	$\frac{\ell - w}{\ell}$	$\frac{\ell - w}{\ell}$	$\frac{h}{h+w}$	y
	$\frac{L_s}{\ell}$	$\frac{L_s}{\ell}$	$\frac{L_s}{h+w}$	z

The universal equations for the zone-void enriching section are:

$$k = \frac{vy}{e^v - 1} \tag{37}$$

and

$$\alpha = \frac{\frac{k - y}{1 - y}}{1 + \frac{1 - k}{k}\left(\frac{vye^{vz}}{1 - e^{v(1-y)}}\right)} \tag{38}$$

For the stripping section of the zone-void system when the freezing in the final zone is assumed to proceed by normal freezing the universal equations are:

$$k = \frac{v}{e^{vy} - 1} \tag{39}$$

and

$$\beta = \frac{e^{vz}(1-ky)}{(1-ky)(1-y)^{1-k} + e^{vz}(1-y) - (1-y)} \tag{40}$$

In the zone-transport enriching section the universal equations are given by

$$k = \frac{vy}{e^{v} - 1} \tag{37}$$

and

$$\alpha = \frac{y - k}{e^{vz}(1-k) + y - 1} \tag{41}$$

The universal equations for the stripping section of the zone-transport system or the zone-void or matter transport systems when the terminal zone undergoes a uniform freeze are

$$k = \frac{v}{e^{vy} - 1} \tag{39}$$

and

$$\beta = \frac{e^{vz}}{1 + \left(\frac{1 - y}{1 - ky}\right)\left(e^{vz} - 1\right)} \qquad (42$$

The four sets of universal equations, Eqs. (37) and (38), Eqs. (39) and (40), Eqs. (37) and (41) and Eqs. (39) and (42) were programmed and run on a high speed digital computer. The computations were made for $k > 1$ as well as for $k < 1$. The y and z values were chosen to give maximum range to the data. Using Eqs. (37) and (39) the families of curves which result from plotting k versus v for several y values are shown in Figures 9 and 10, respectively. For plots of α or β versus k each y value used generated a family of z curves. There were seven y values used for each of the four cases. For $k < 1$ the twenty-eight families of z curves which resulted are shown in Figures 11-38 inclusive. Figures 11-17 show α versus k when Eq. (38) is used, Figures 18-24 are plots of β versus k when Eq. (40) is run, Figures 25-31 are the α versus k plots of Eq. (41) and Figures 32-38 show the β versus k curves when Eq. (42) is used.

A comparison of Figures 11-17 with Figures 25-31 reveals that the effect of the difference in the definition of the solute concentration in the product on the value of α increases with decreasing z. However, for $z > 5$ the value of α for both cases is almost identical.

A comparison of Figures 18-24 with Figures 32-38 permits an evaluation of the effect of assuming a normal or uniform freeze in the final zone of a stripping section. It is readily seen that for $z = 2$ the normal freeze section provides a slightly better separation than the uniform freeze, however, for all other values of z the values of β are essentially identical.

The functions of the respective sections of a zone-refining system when $k < 1$ are reversed when $k > 1$; thus, the stripping section becomes the enriching section and vice versa. Graphs of k versus α or β for each set of universal equations when $k > 1$ are shown in Figures 39-66. Thus:

1. Figures 39-45 are plots of α versus k when Eq. (38) is used.
2. Figures 46-52 are plots of β versus k when Eq. (40) is used.
3. Figures 53-59 are plots of α versus k when Eq. (41) is used.
4. Figures 60-66 are plots of β versus k when Eq. (42) is used.

A comparison similar to those made with Figures 11-38 can be made with Figures 39-66.

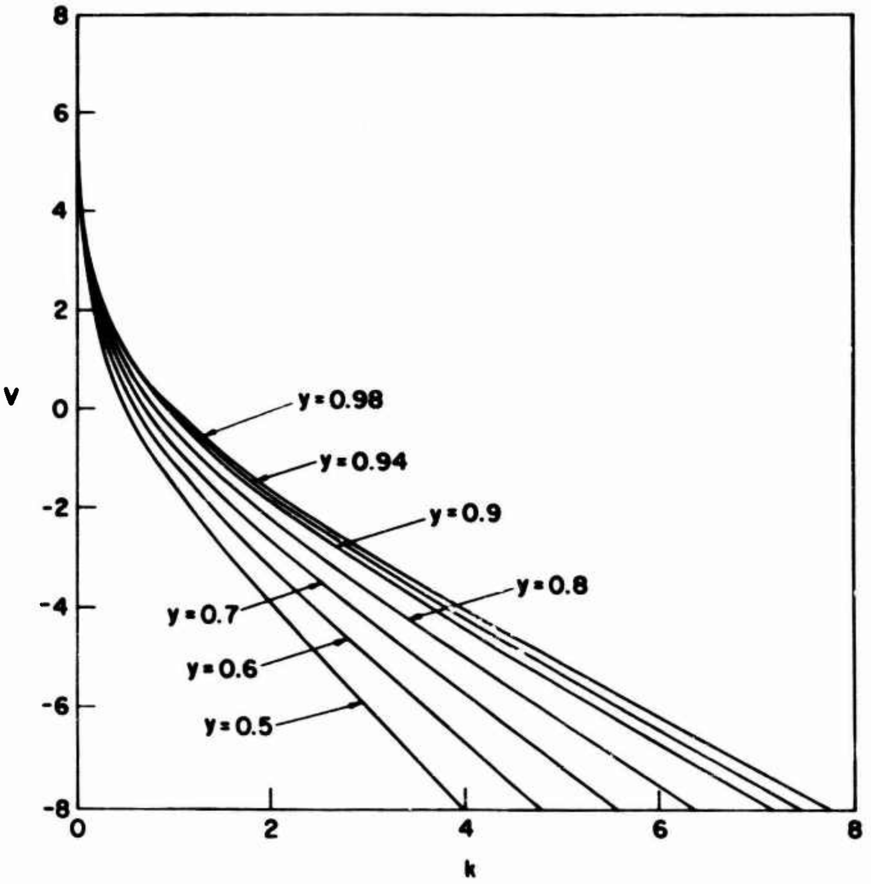

Figure 9. Plot of k vs v Using Eq. (37)

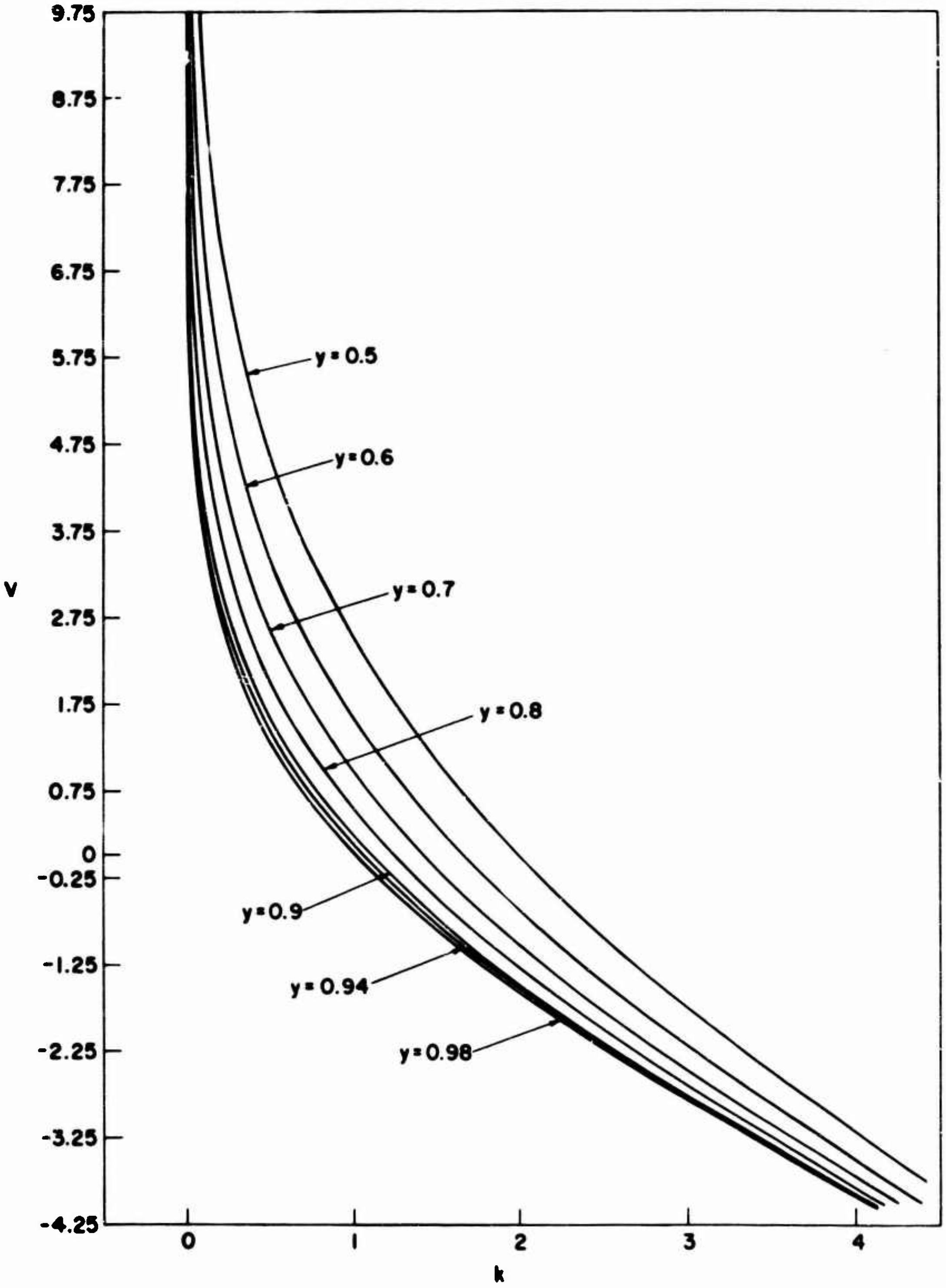

Figure 10. Plot of k vs v Using Eq. (39)

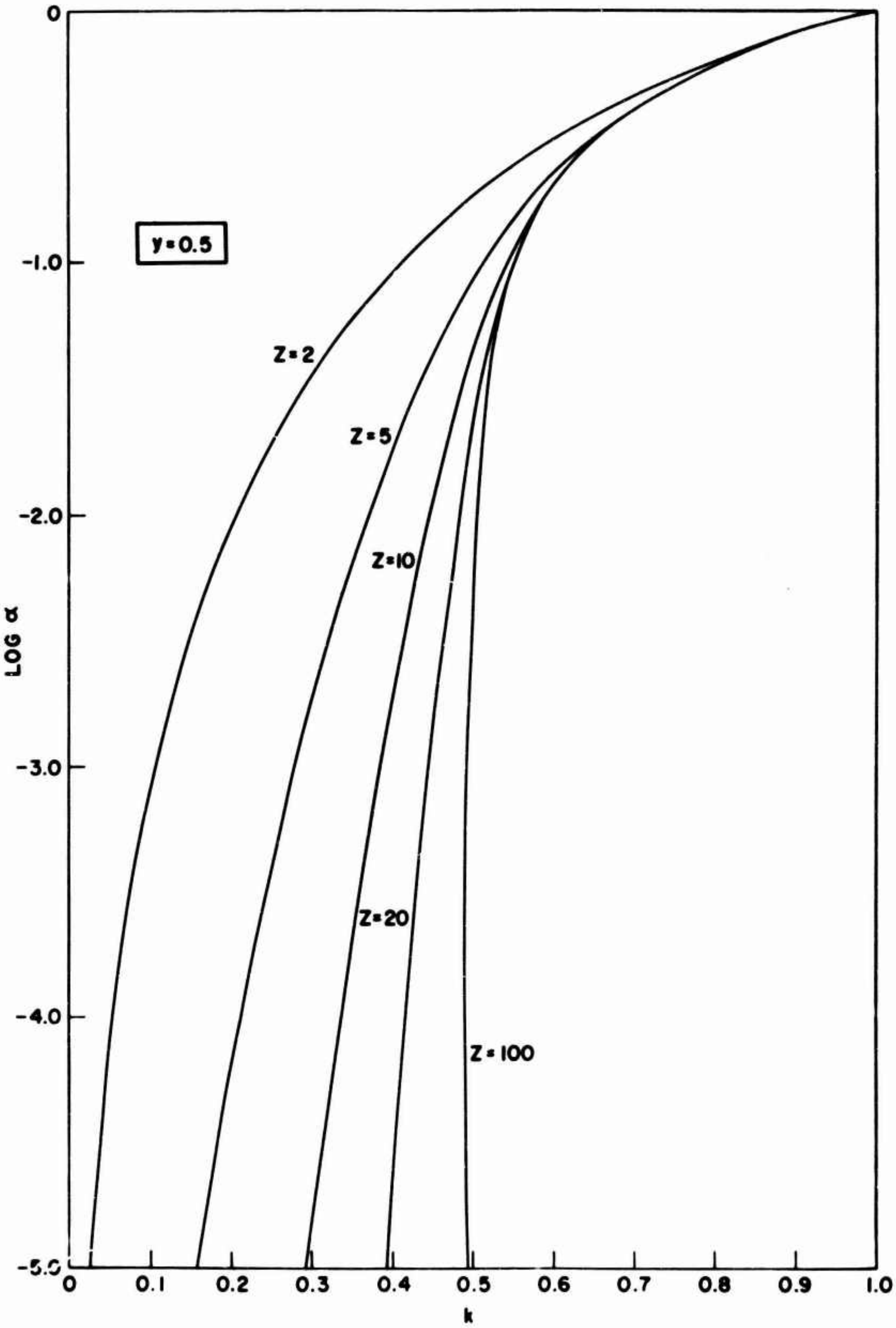

Figure 11. Plot of log a vs k when Eq. (38) is Used and k < 1

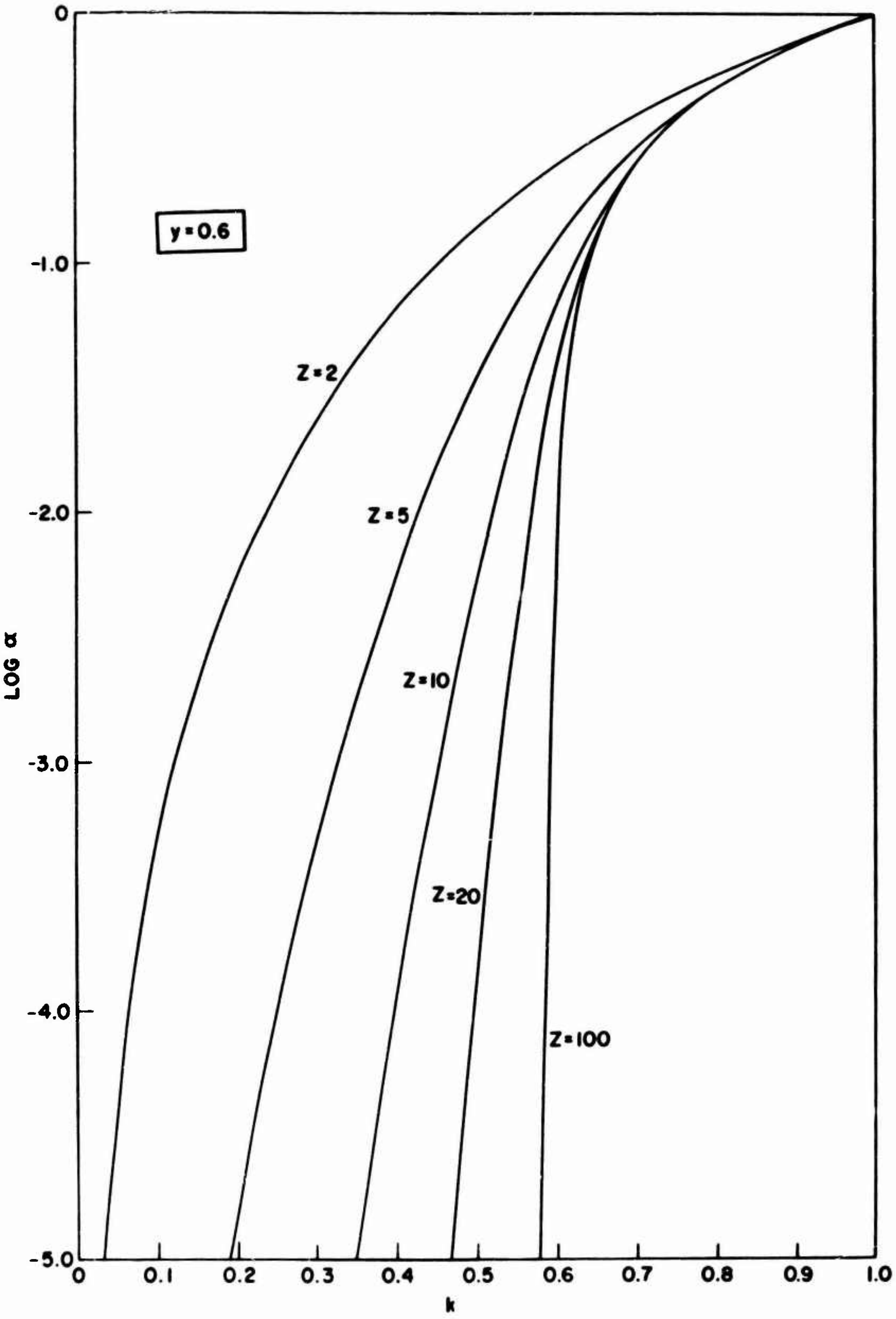

Figure 12. Plot of log α vs k when Eq. (38) is Used and k < 1

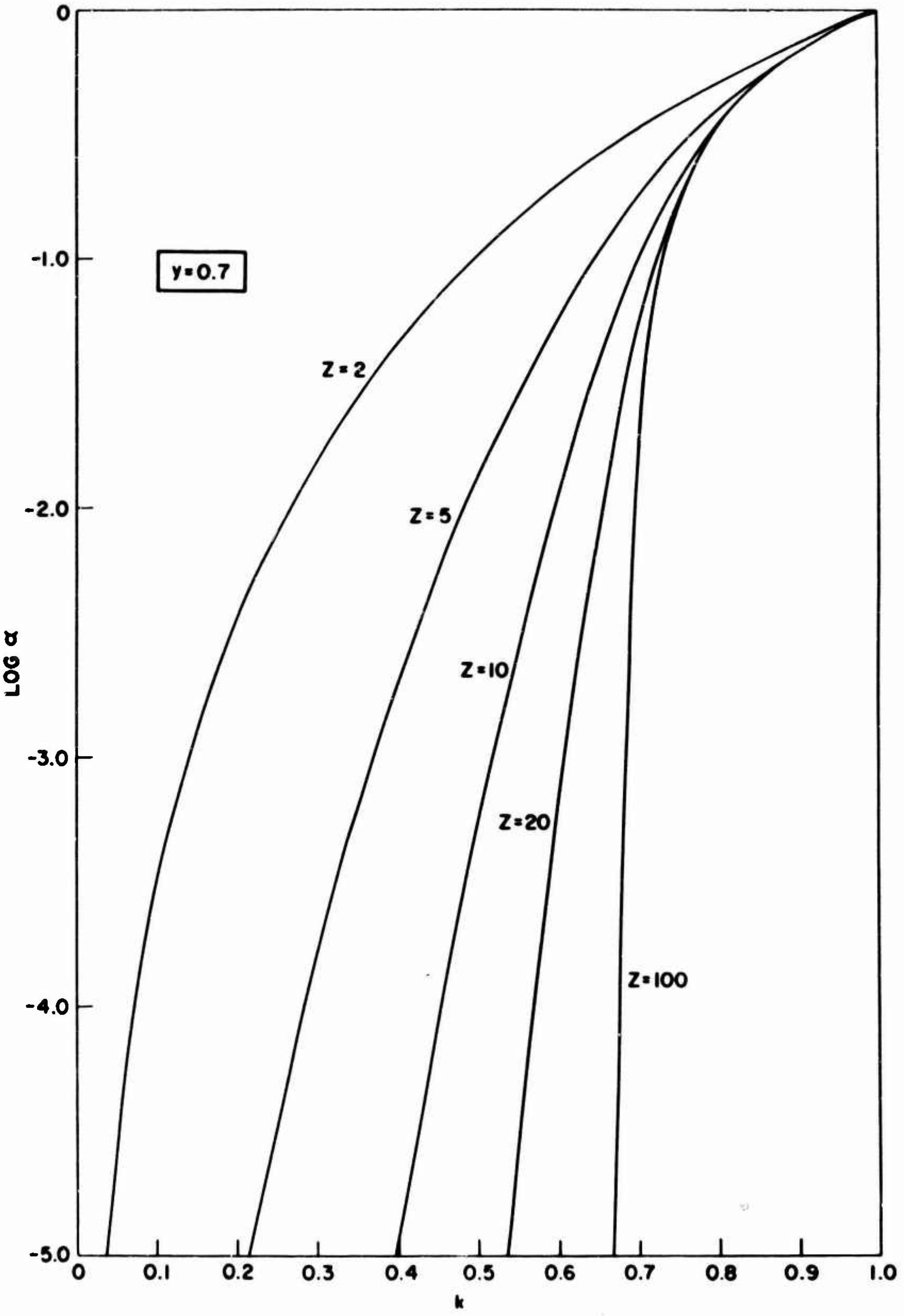

Figure 13. Plot of log α vs k when Eq. (38) is Used and k < 1

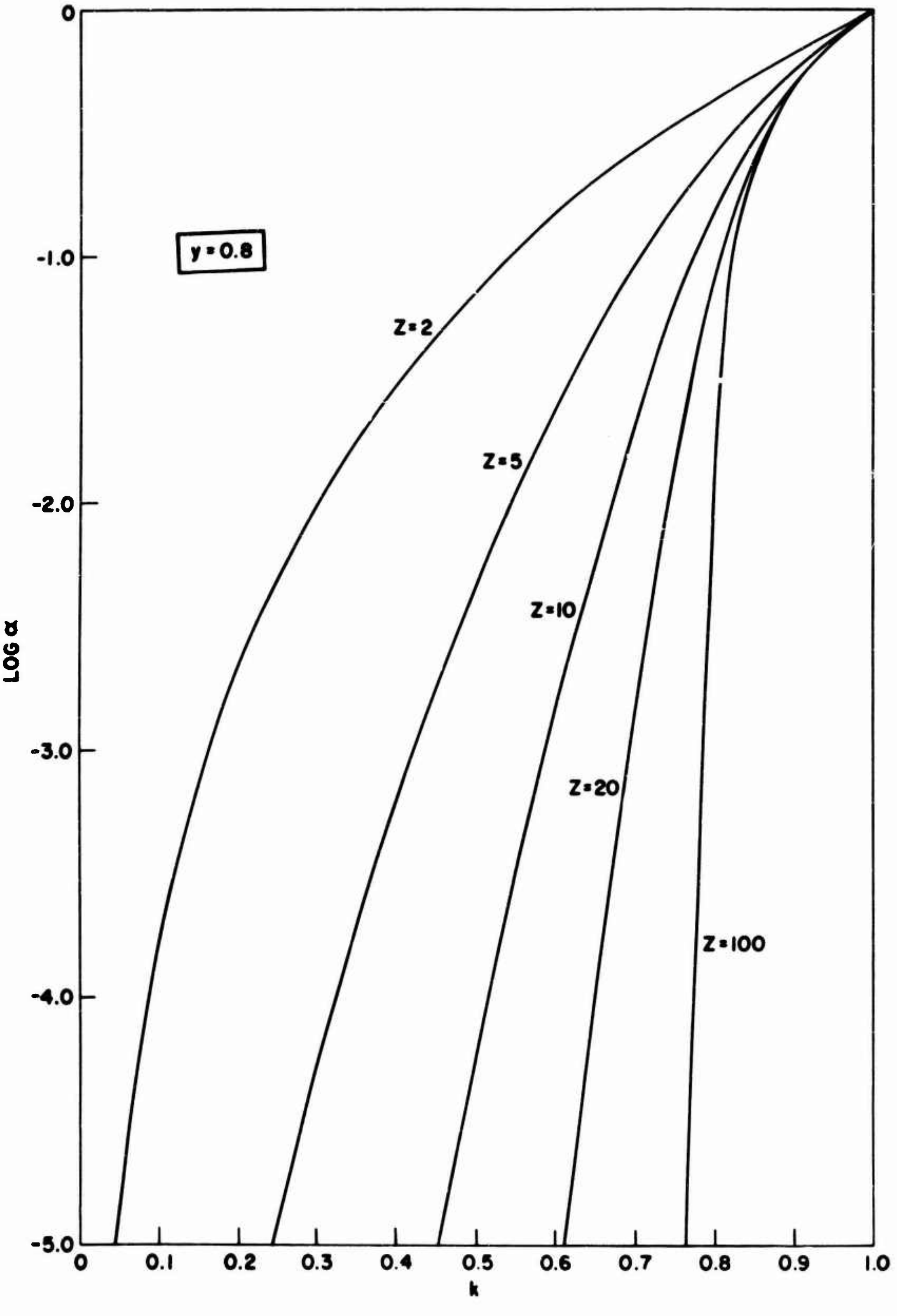

Figure 14. Plot of log α vs k when Eq. (38) is Used and $k < 1$

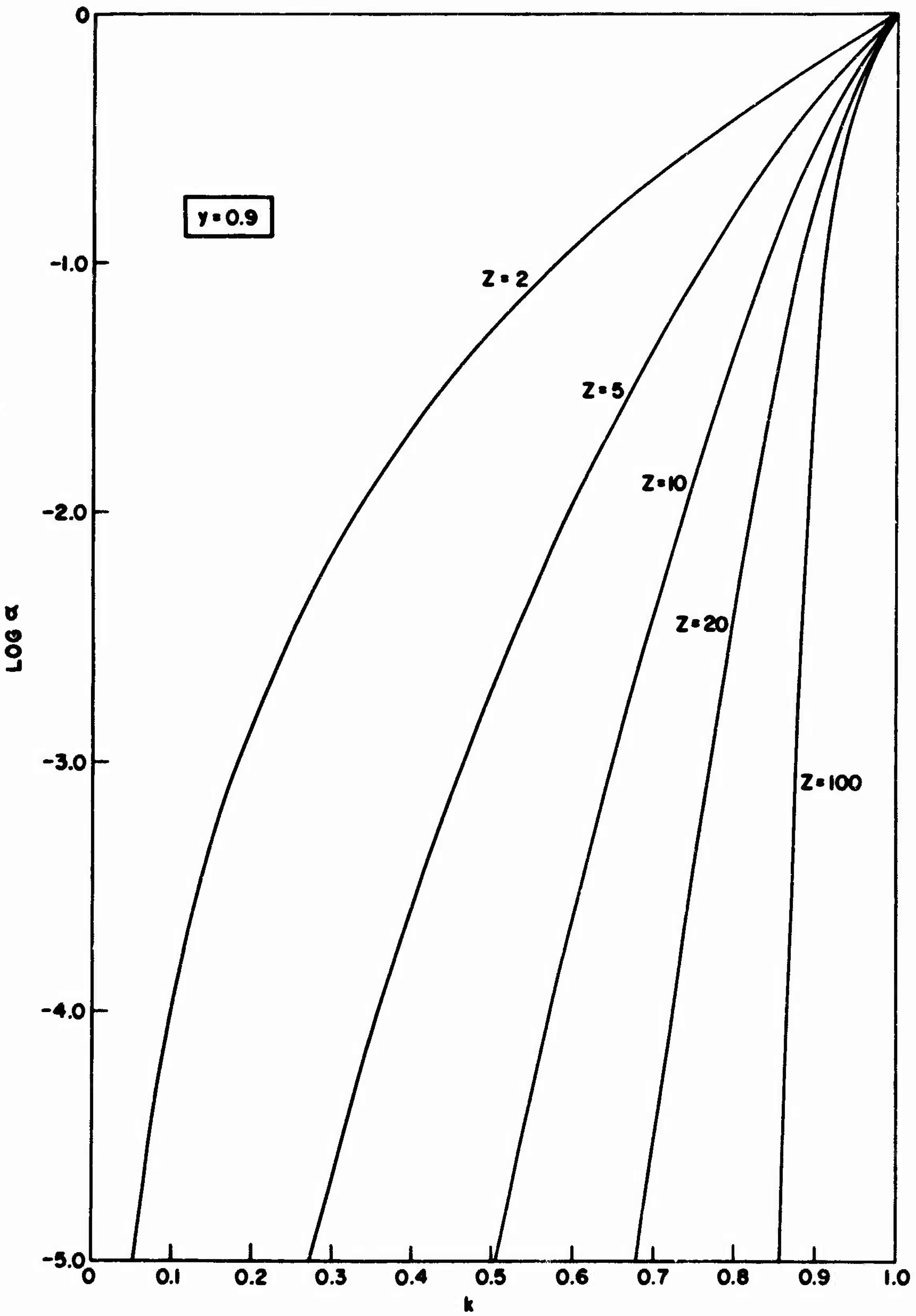

Figure 15. Plot of log α vs k when Eq. (38) is Used and k < 1

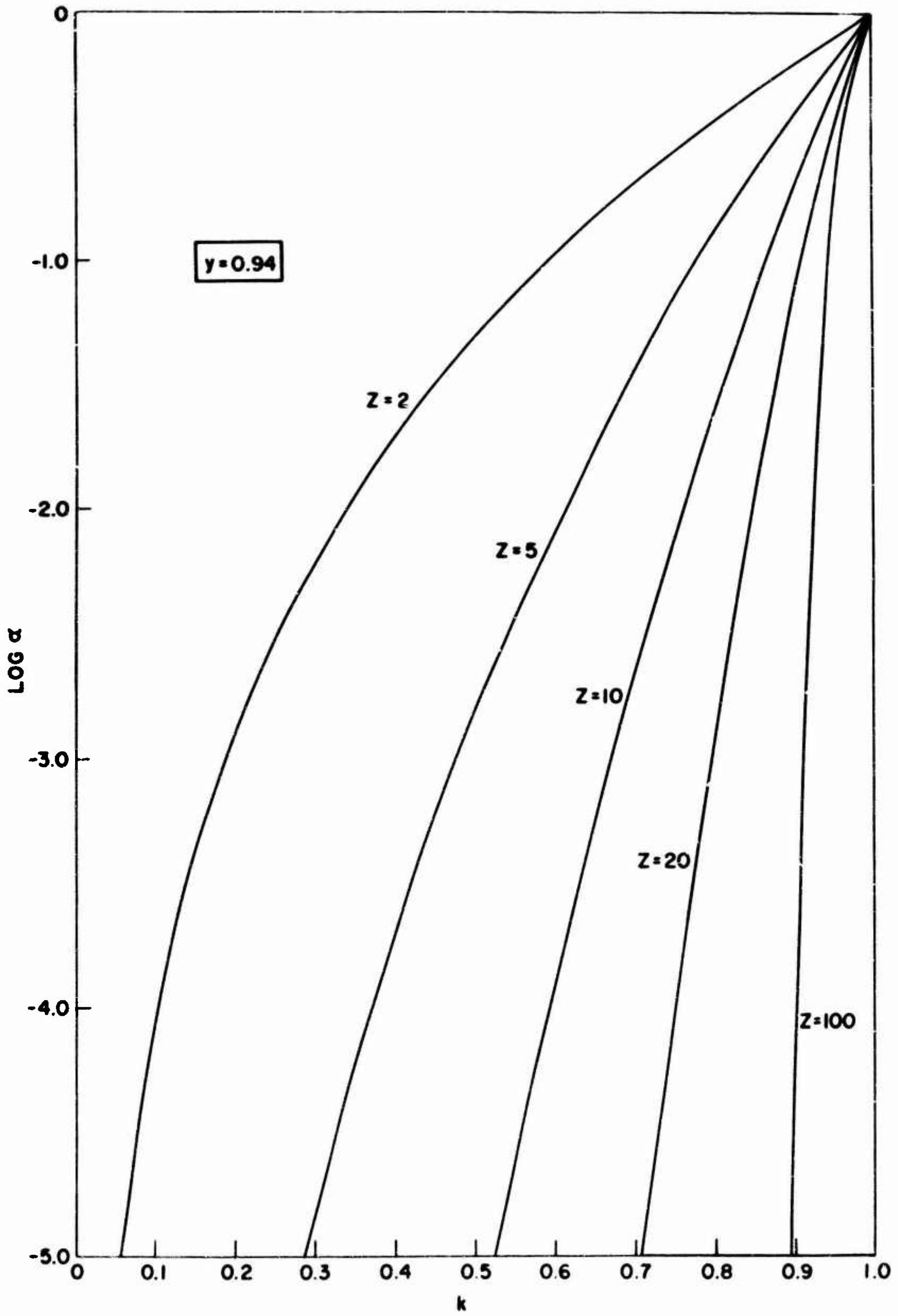

Figure 16. Plot of log α vs k when Eq. (38) is Used and k < 1

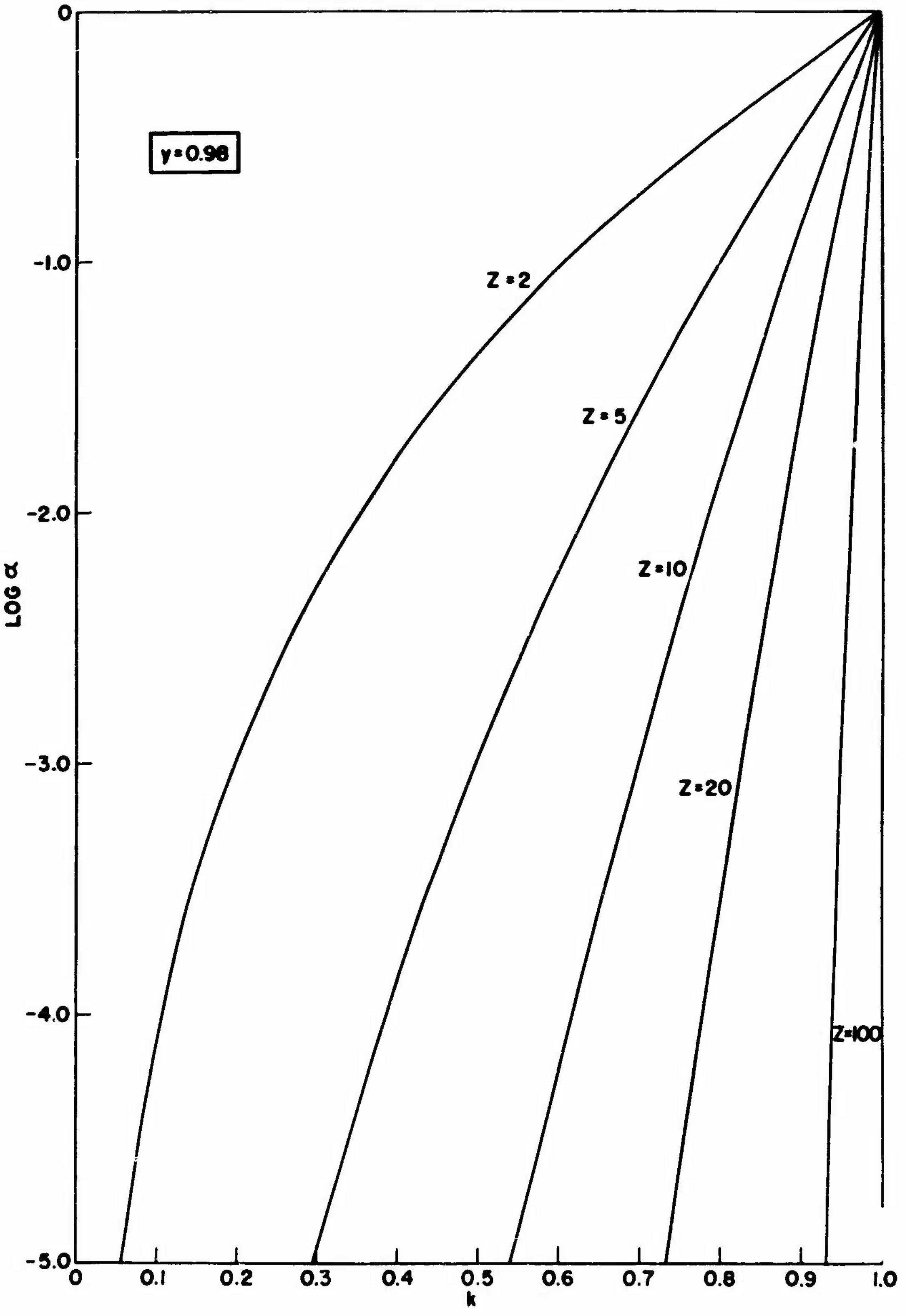

Figure 17. Plot of log α vs k when Eq. (38) is Used and k < 1

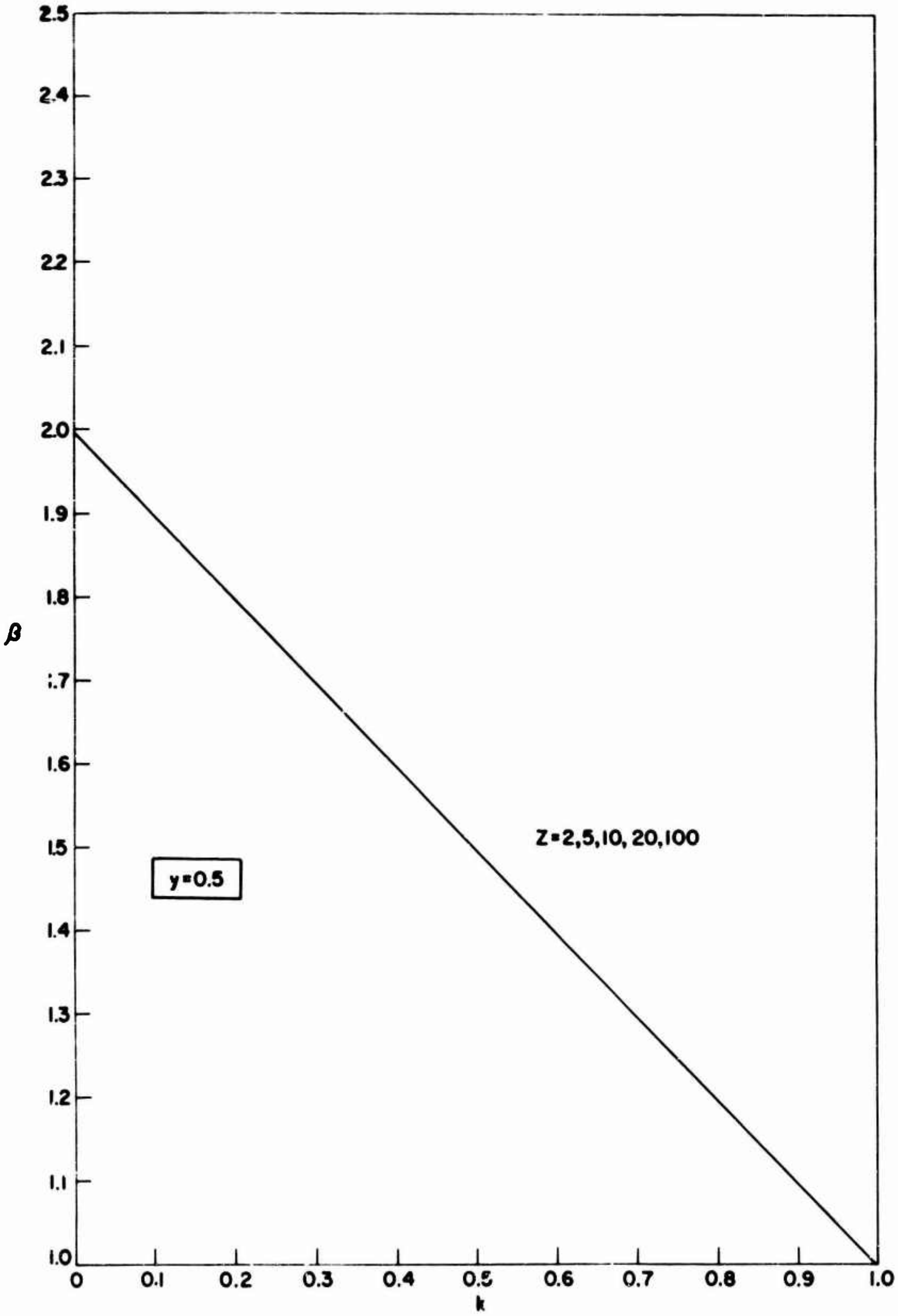

Figure 18. Plot of β vs k when Eq. (40) is Used and k < 1

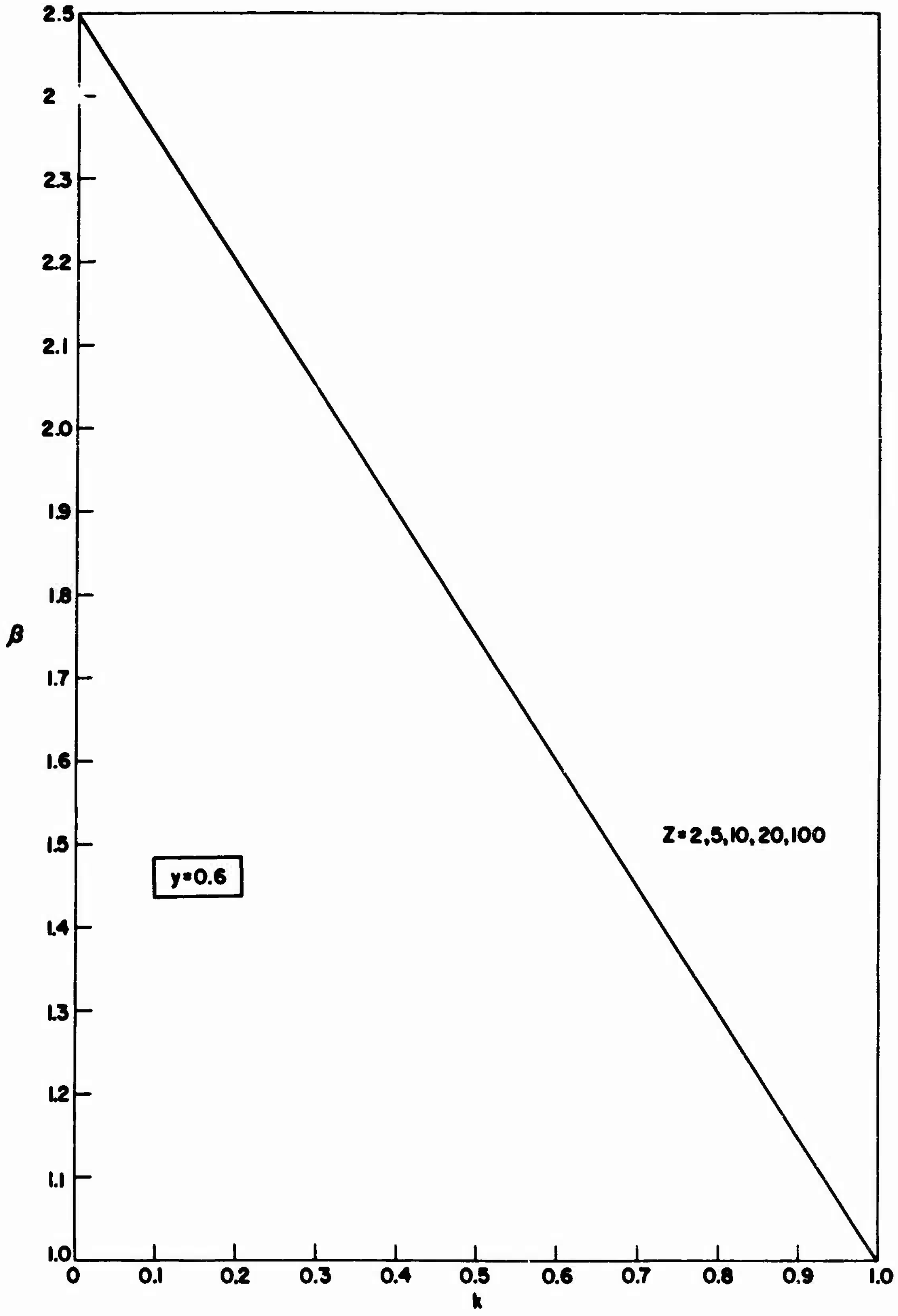

Figure 19. Plot of β vs k when Eq. (40) is Used and k < 1

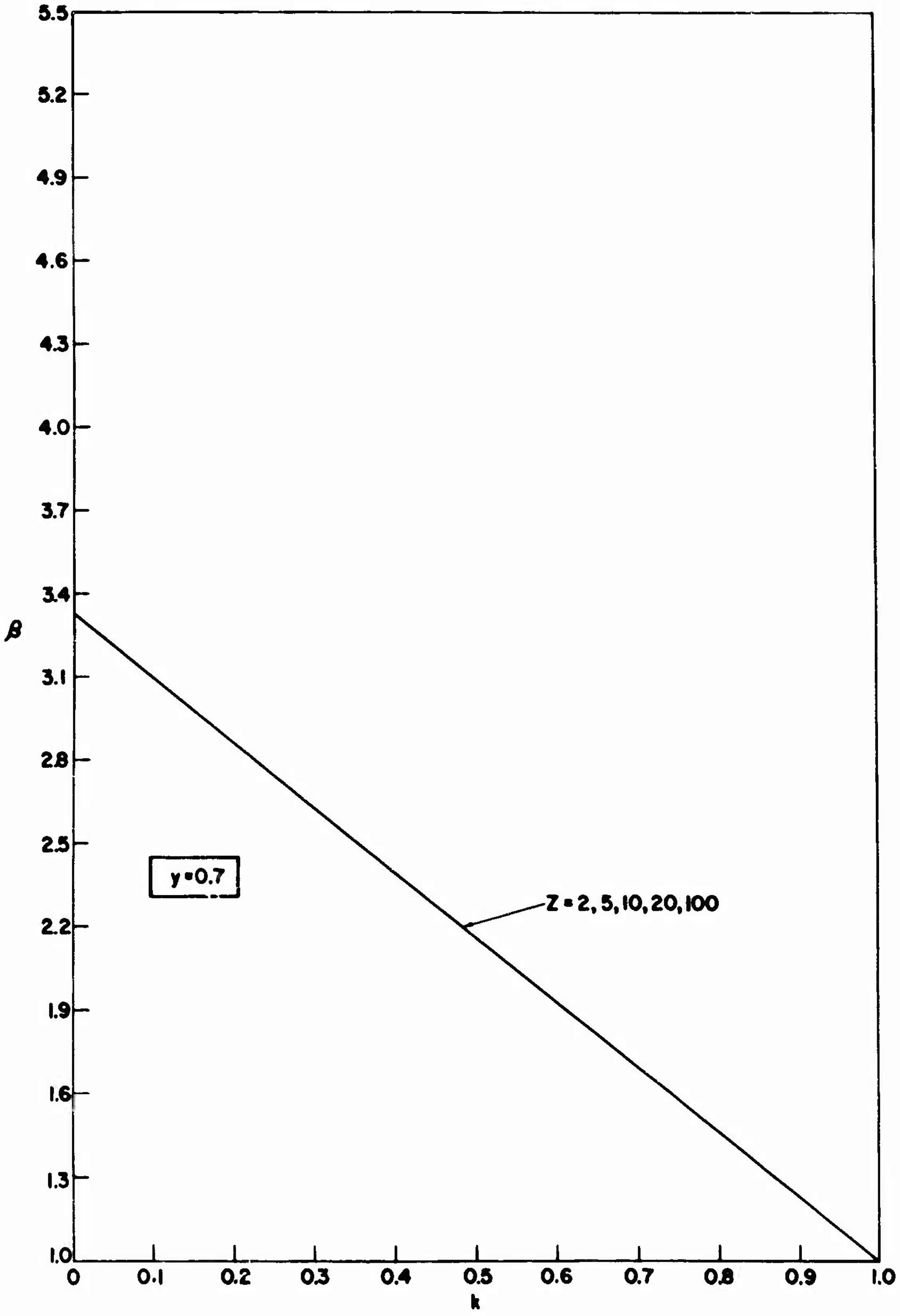

Figure 20. Plot of β vs k when Eq. (40) is Used and k < 1

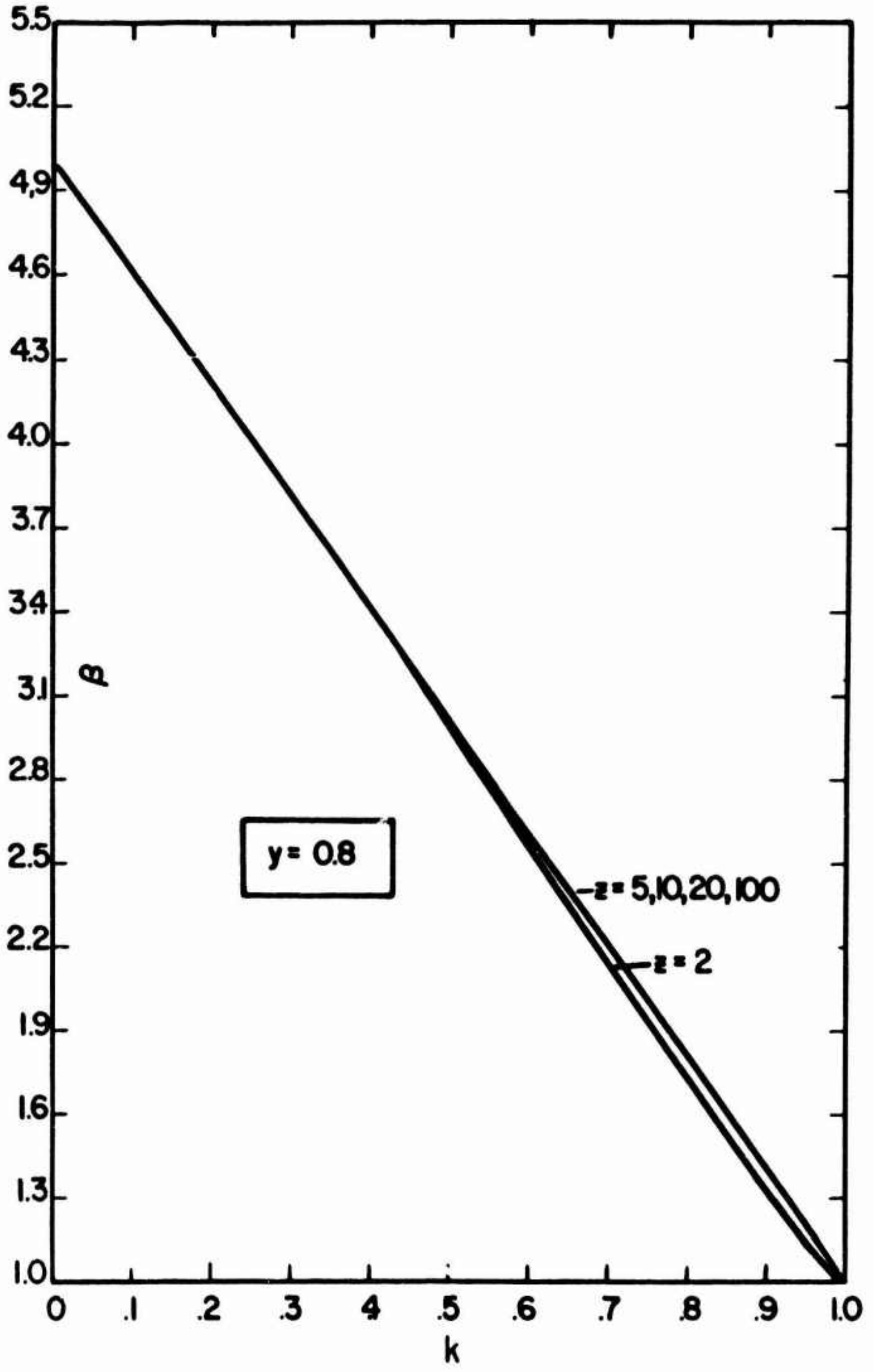

Figure 21. Plot of β vs k when Eq. (40) is Used and k < 1

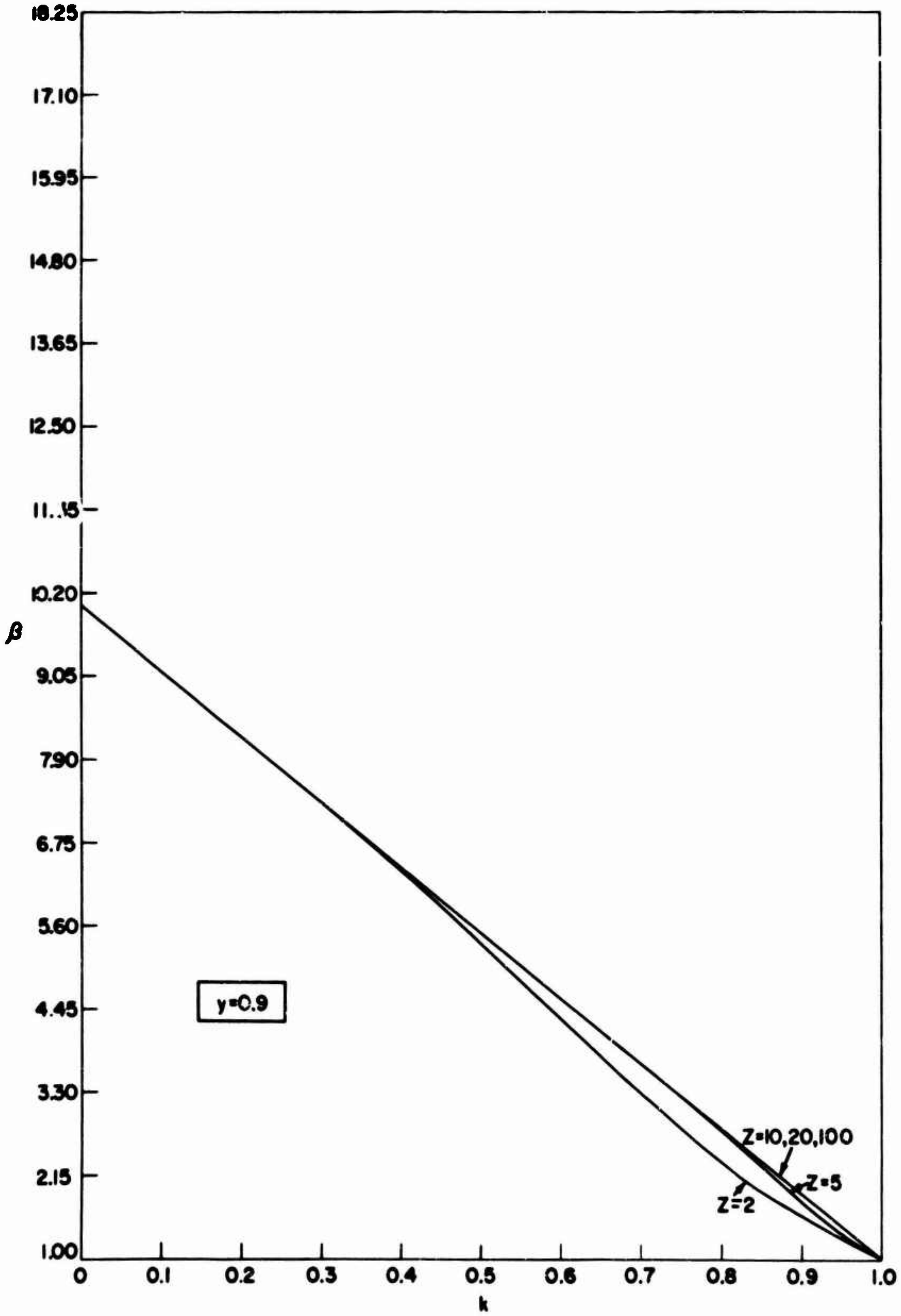

Figure 22. Plot of β vs k when Eq. (40) is Used and k < 1

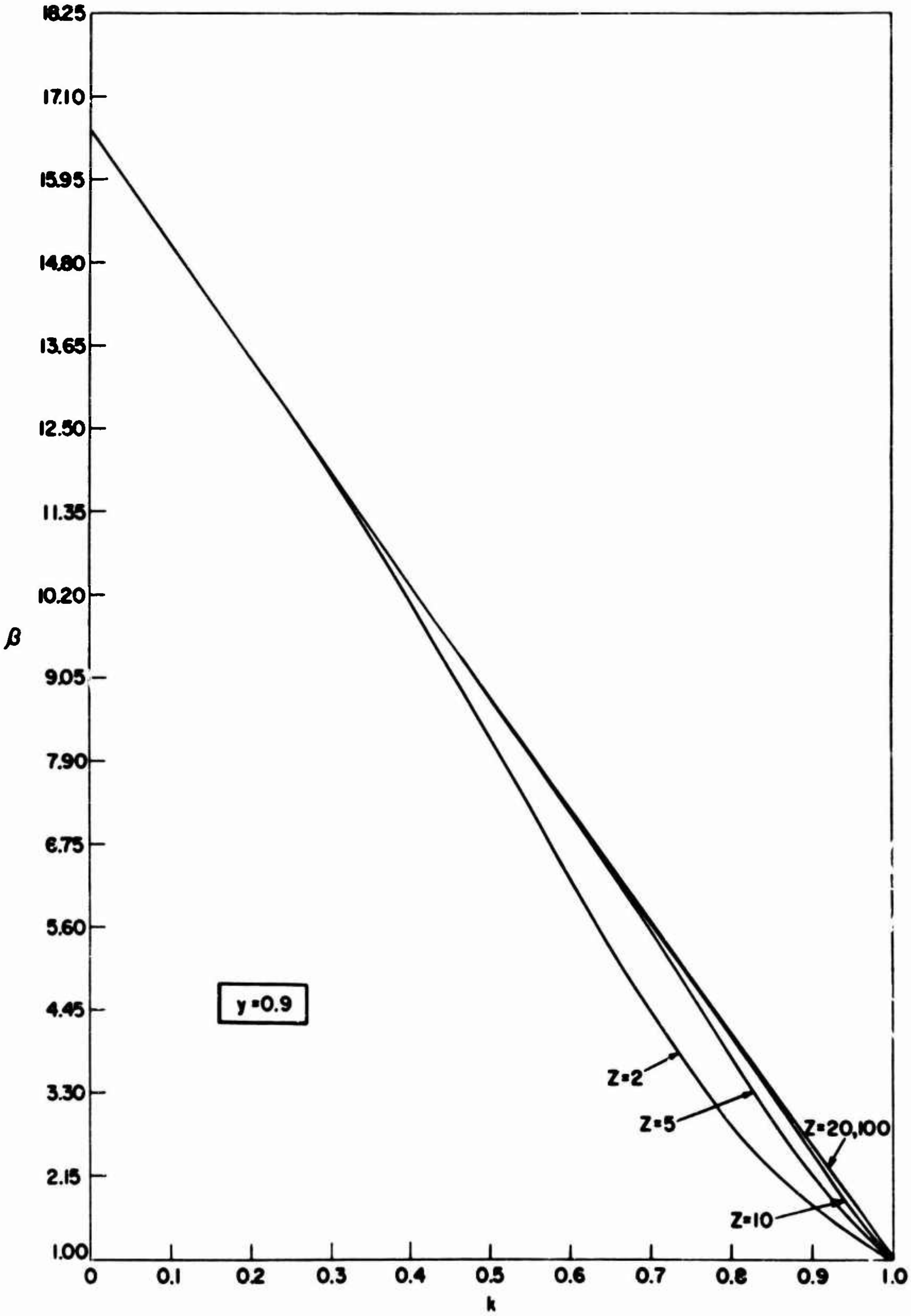

Figure 23. Plot of β vs k when Eq. (40) is Used and k < 1

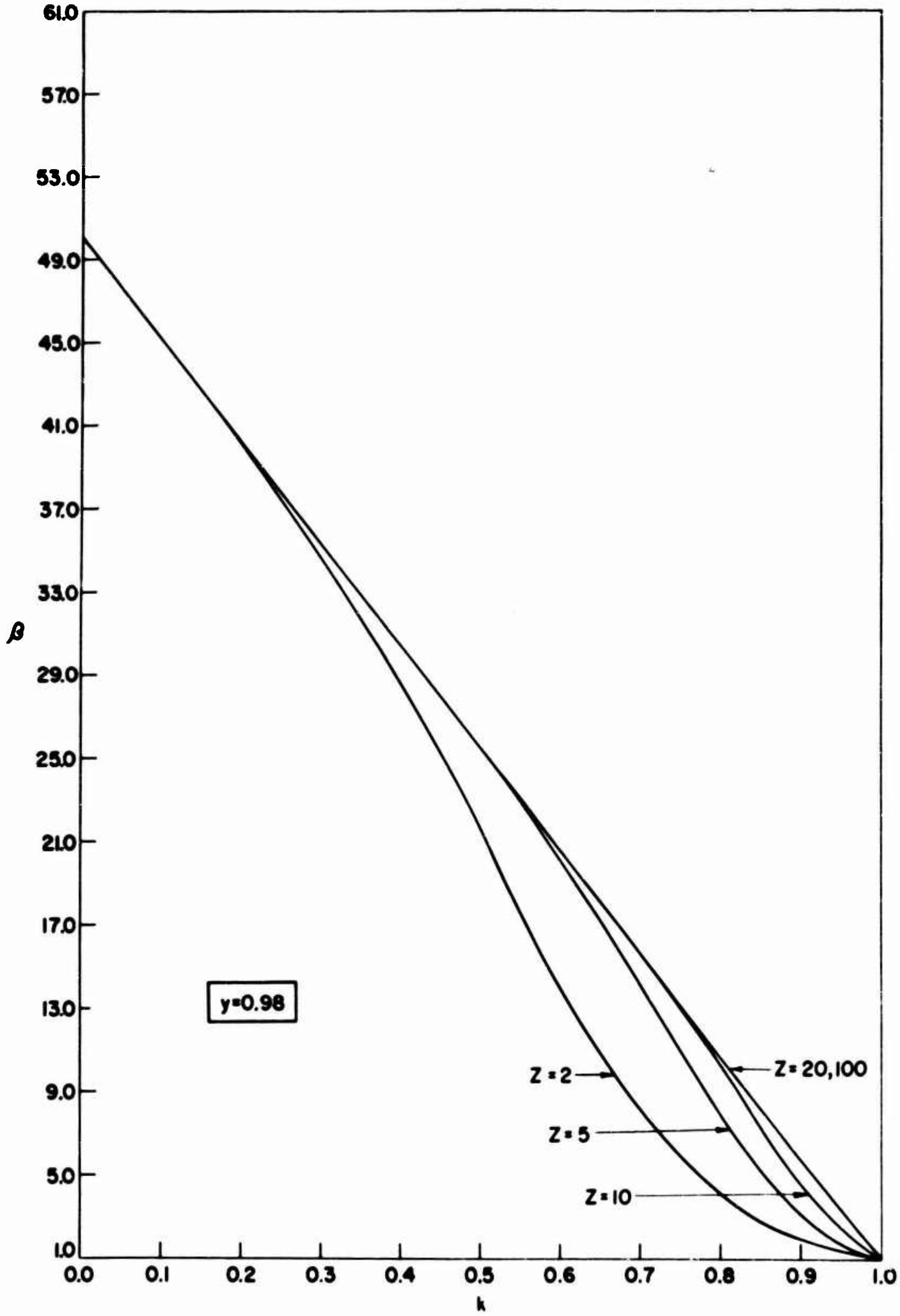

Figure 24. Plot of β vs k when Eq. (40) is Used and k < 1

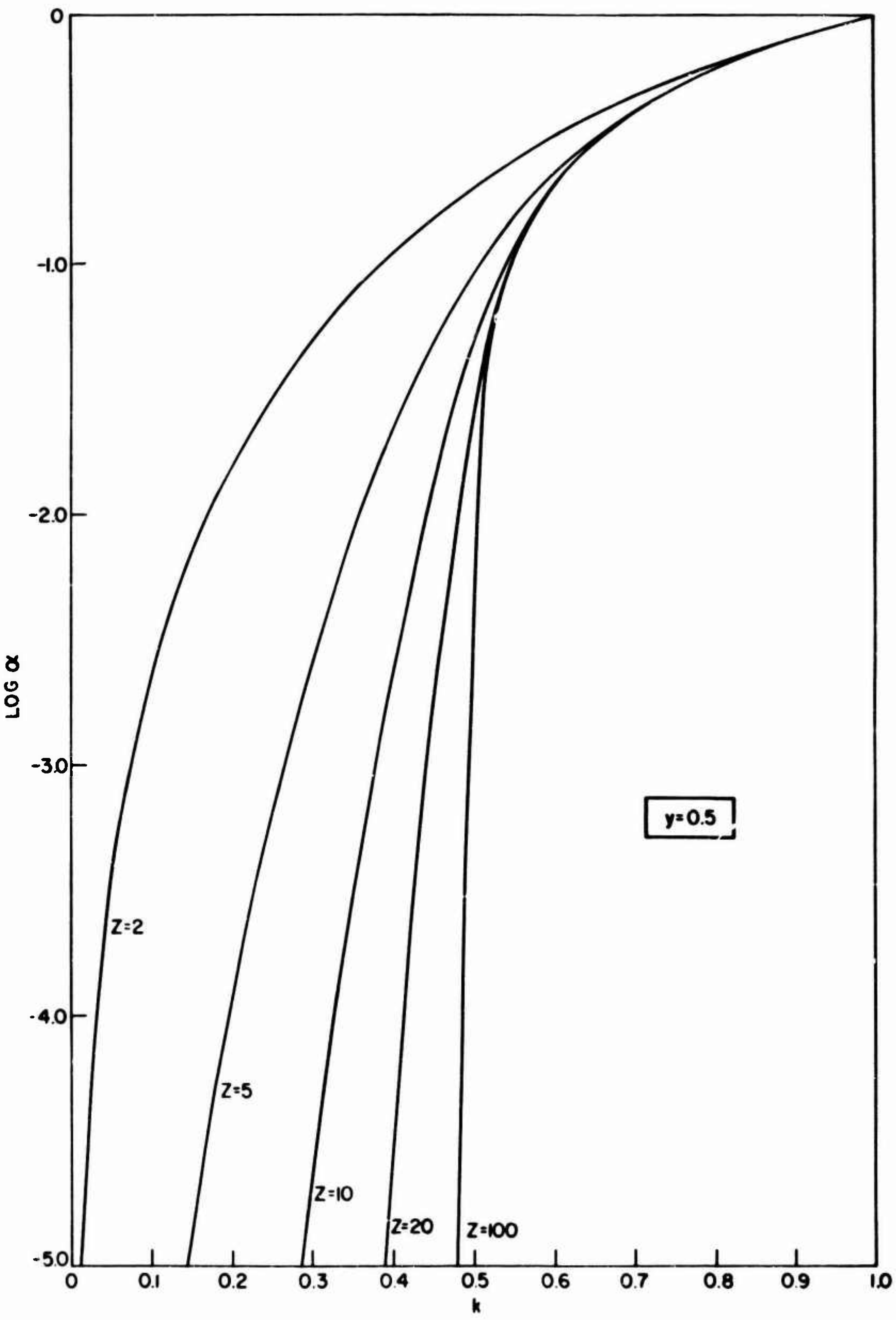

Figure 25. Plot of log α vs k when Eq. (41) is Used and k < 1

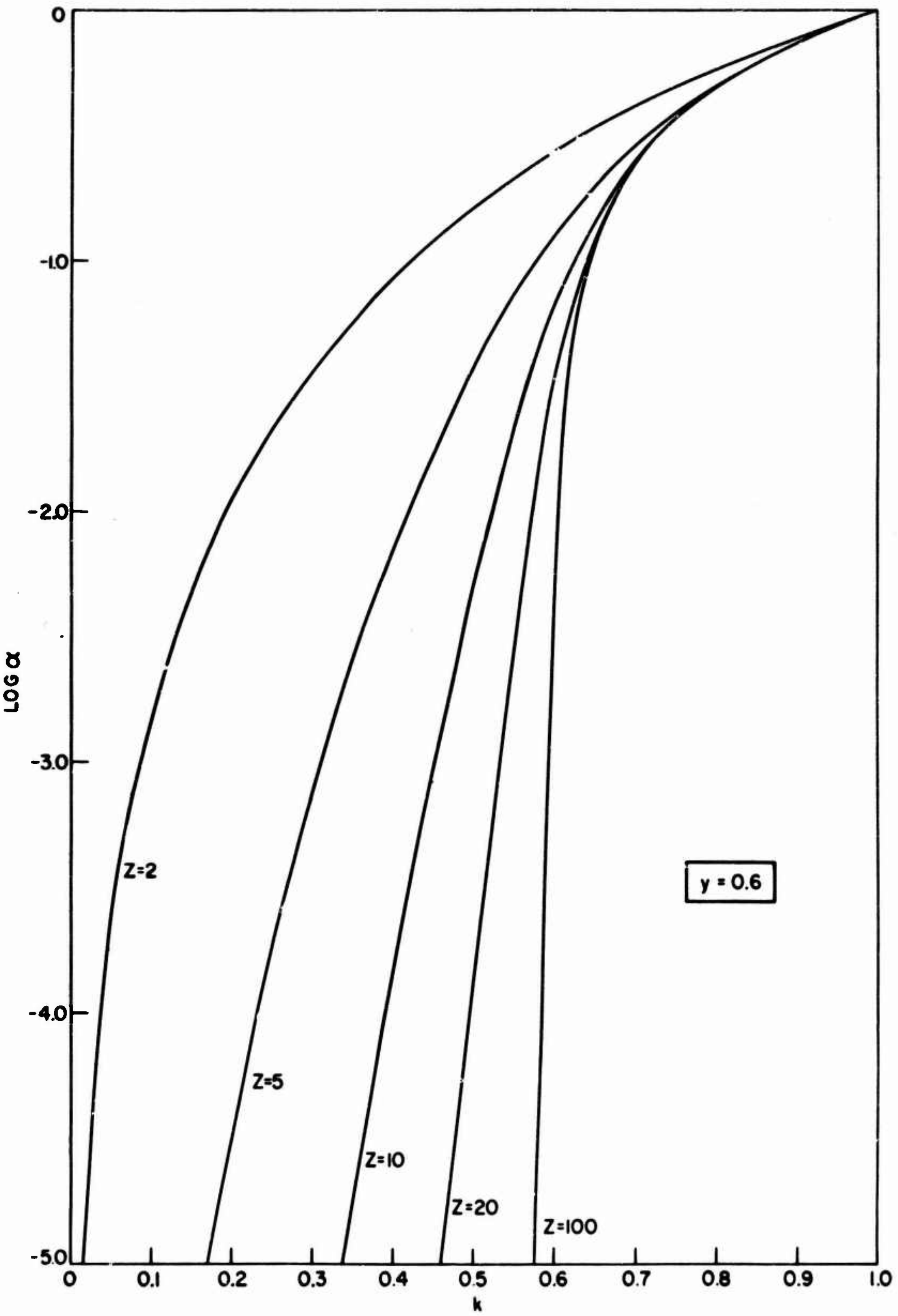

Figure 26. Plot of log α vs k when Eq. (41) is Used and k < 1

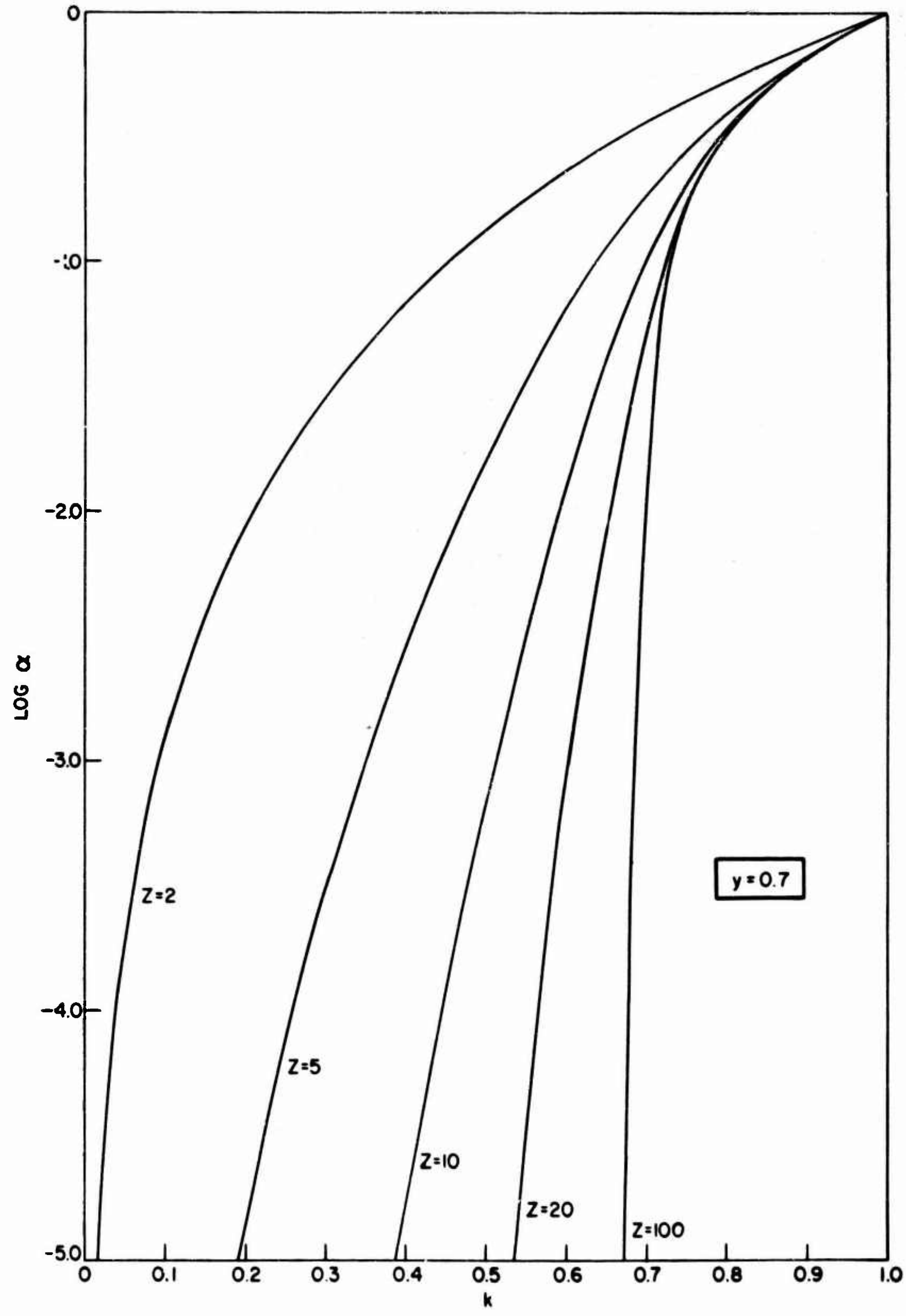

Figure 27. Plot of log α vs k when Eq. (41) is Used and $k < 1$

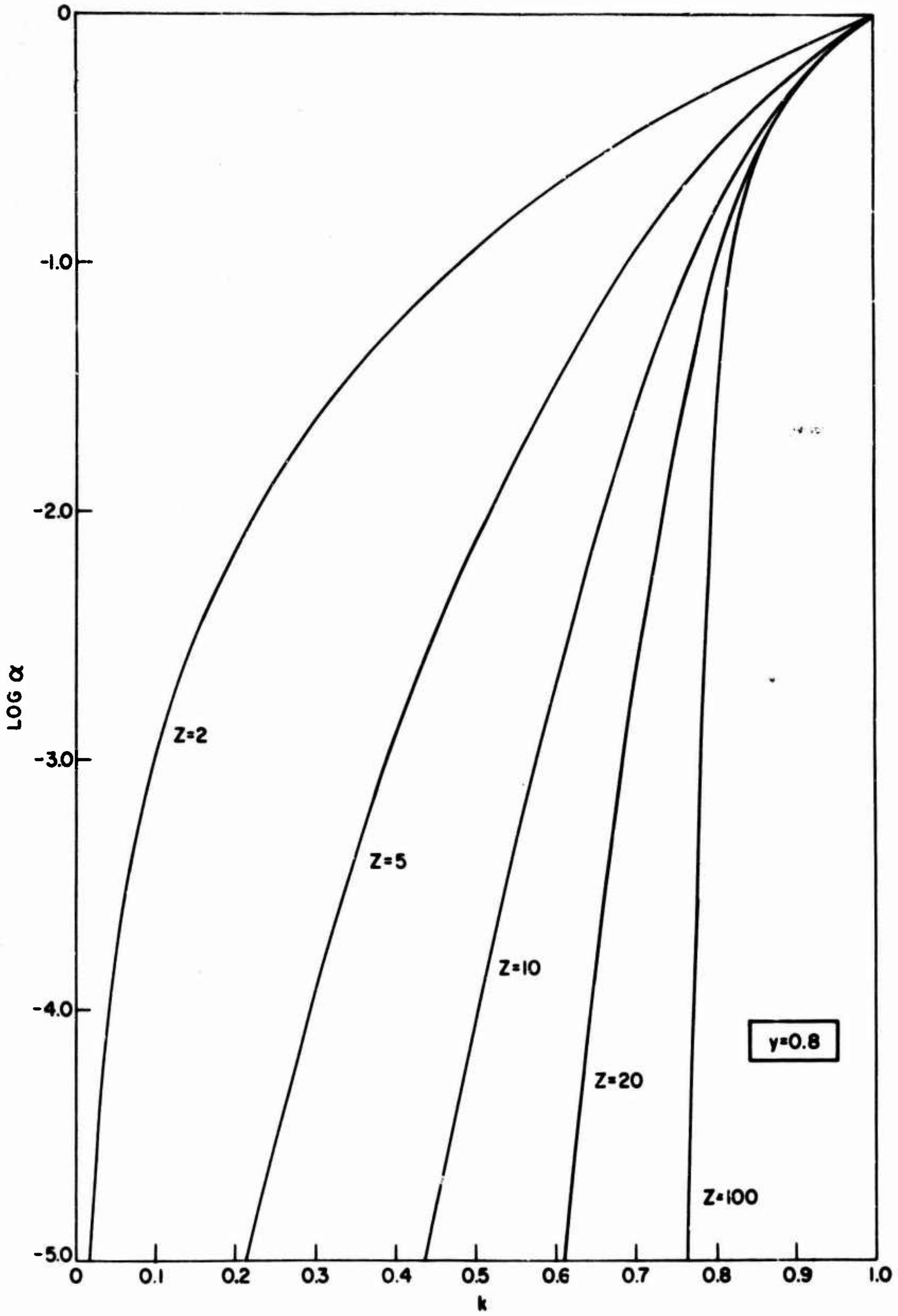

Figure 28. Plot of log α vs k when Eq. (41) is Used and k < 1

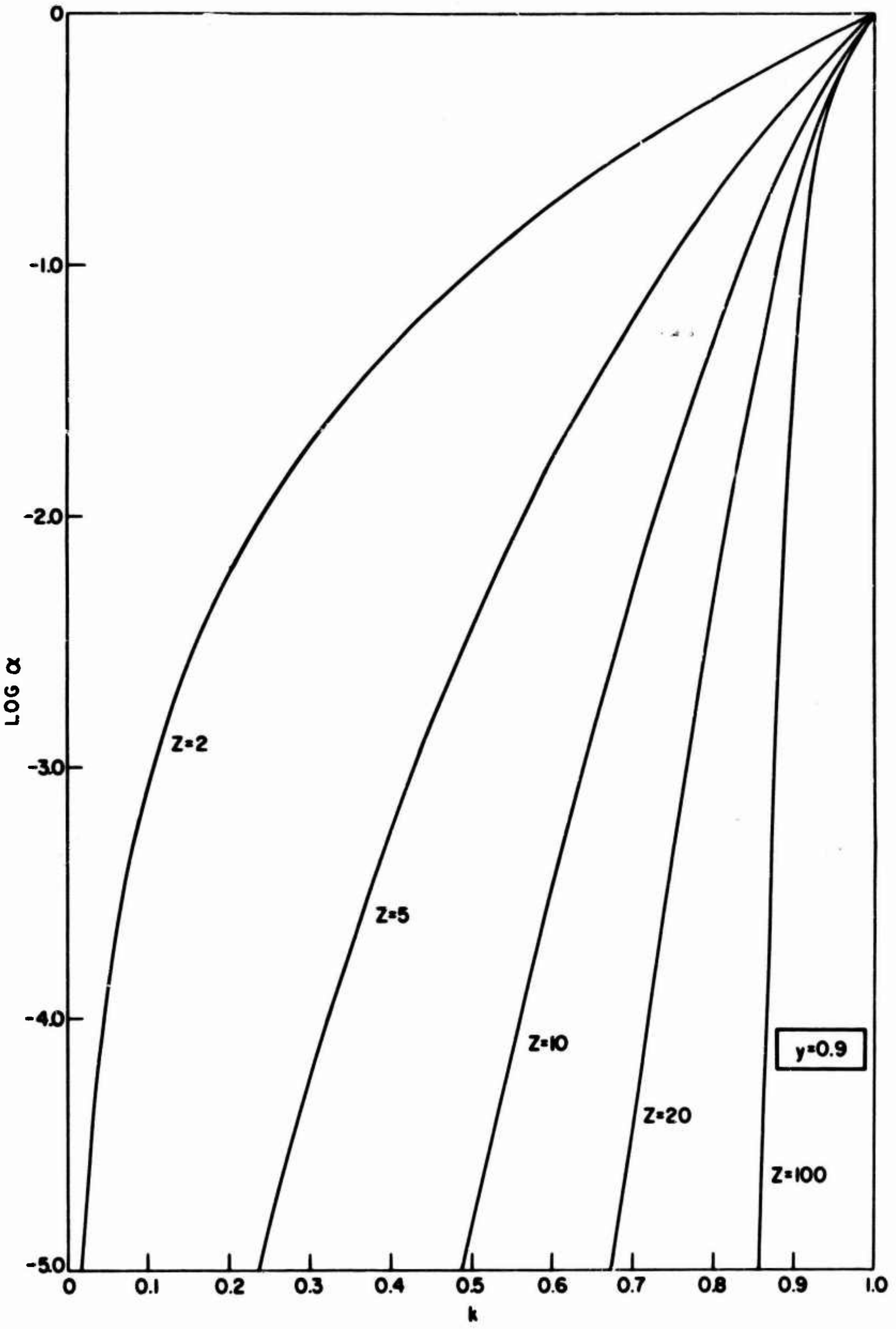

Figure 29. Plot of log α vs k when Eq. (41) is Used and k < 1

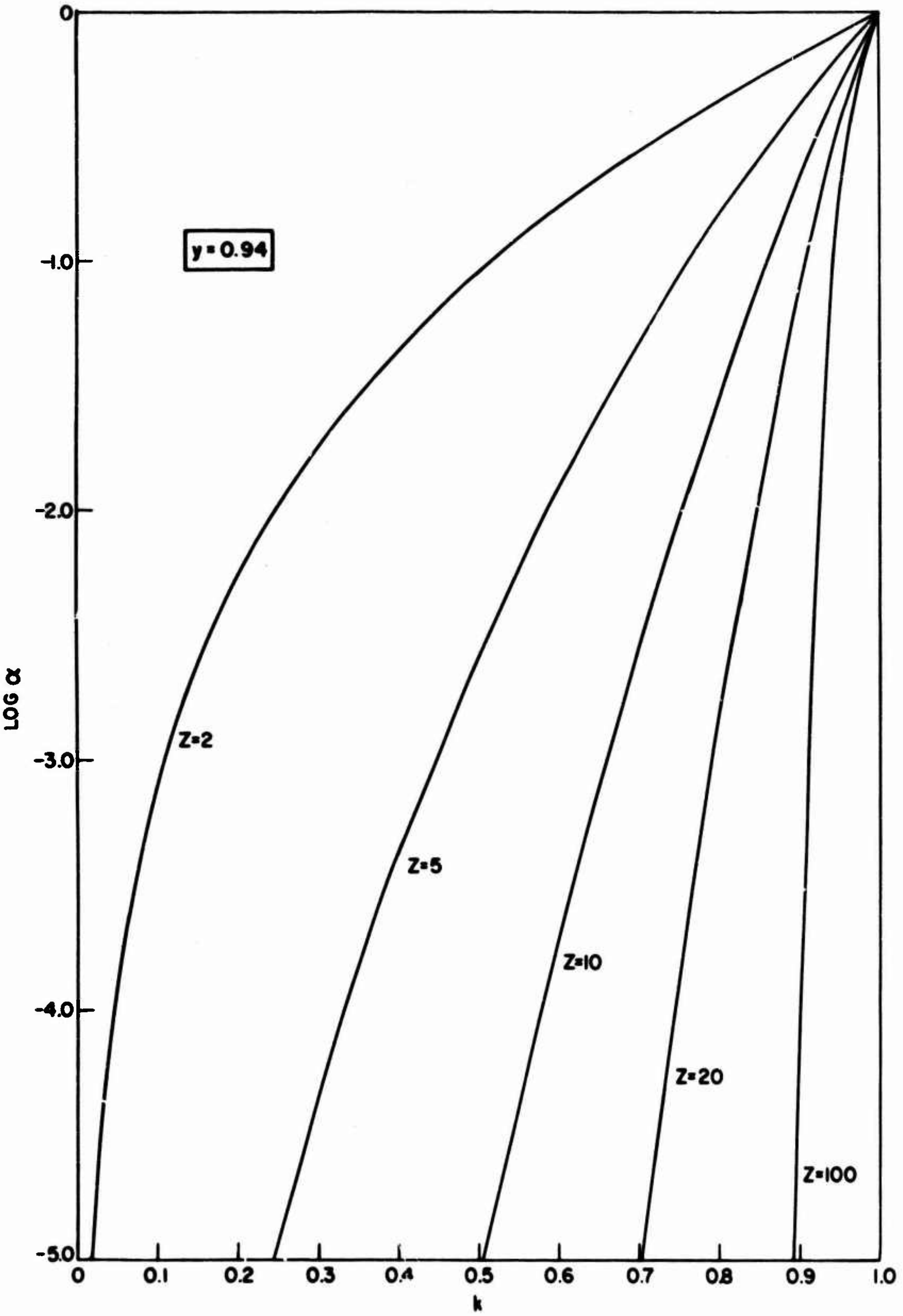

Figure 30. Plot of log α vs k when Eq. (41) is Used and $k < 1$

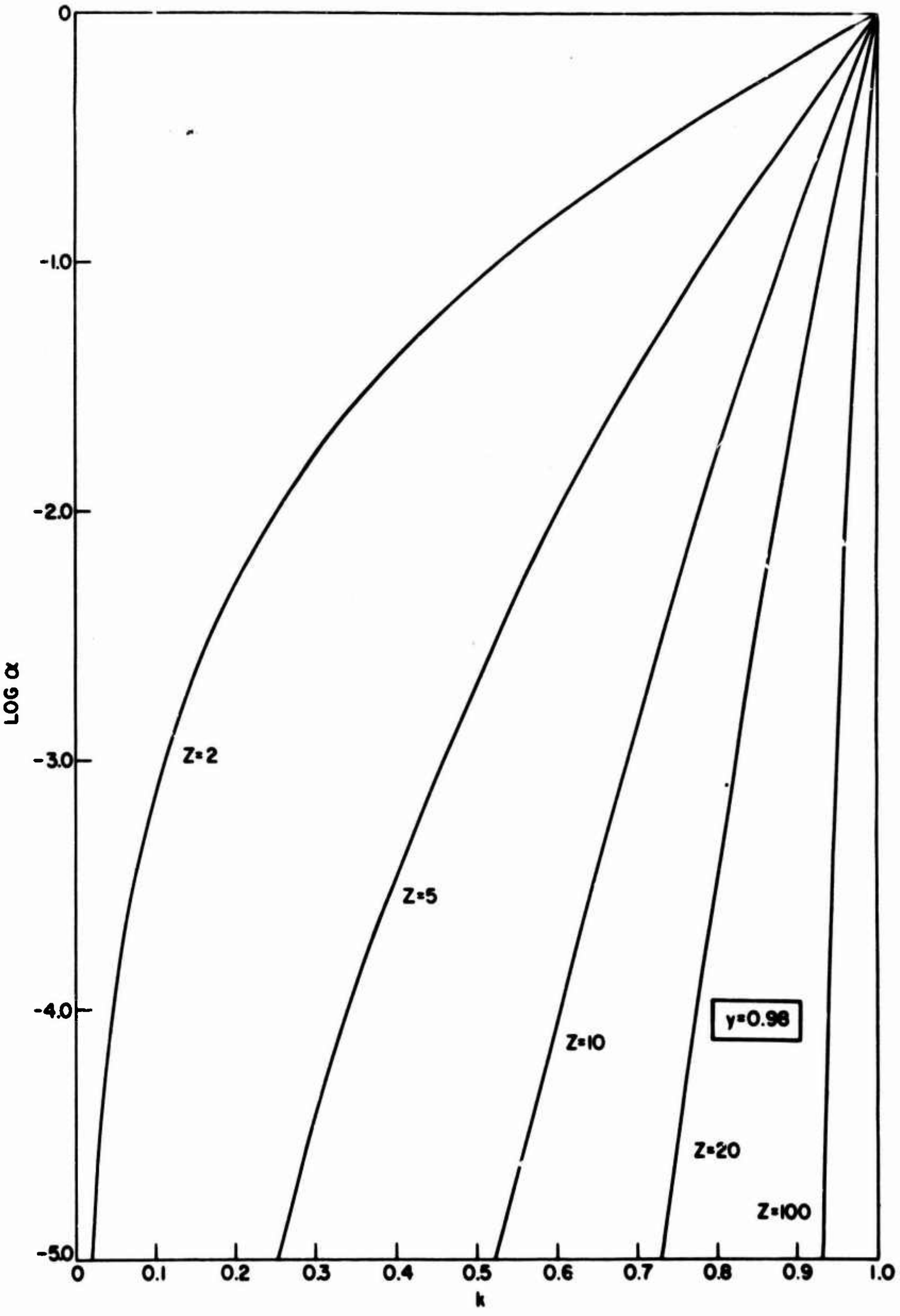

Figure 31. Plot of log α vs k when Eq. (41) is Used and k < 1

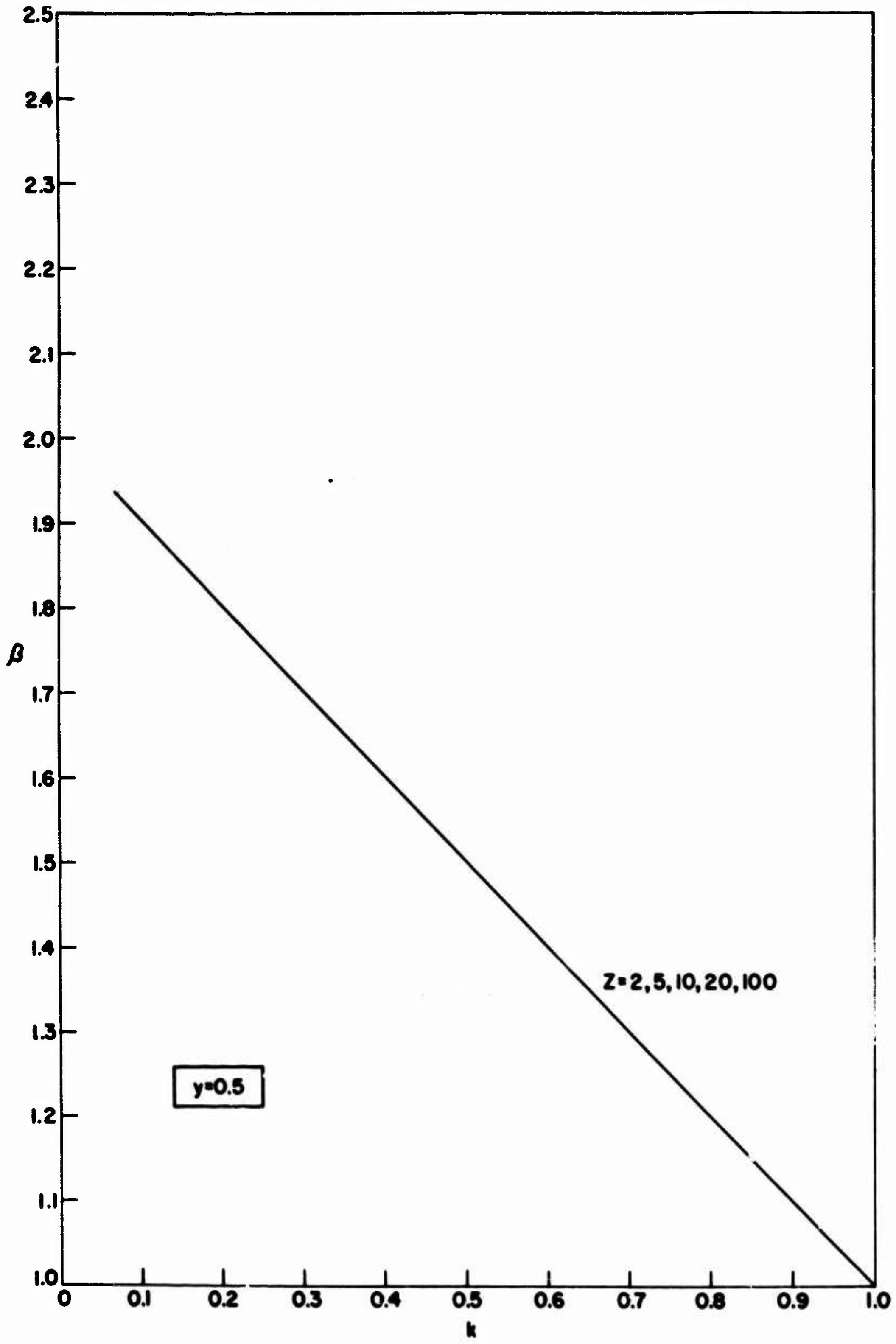

Figure 32. Plot of β vs k when Eq. (42) is Used and k < 1

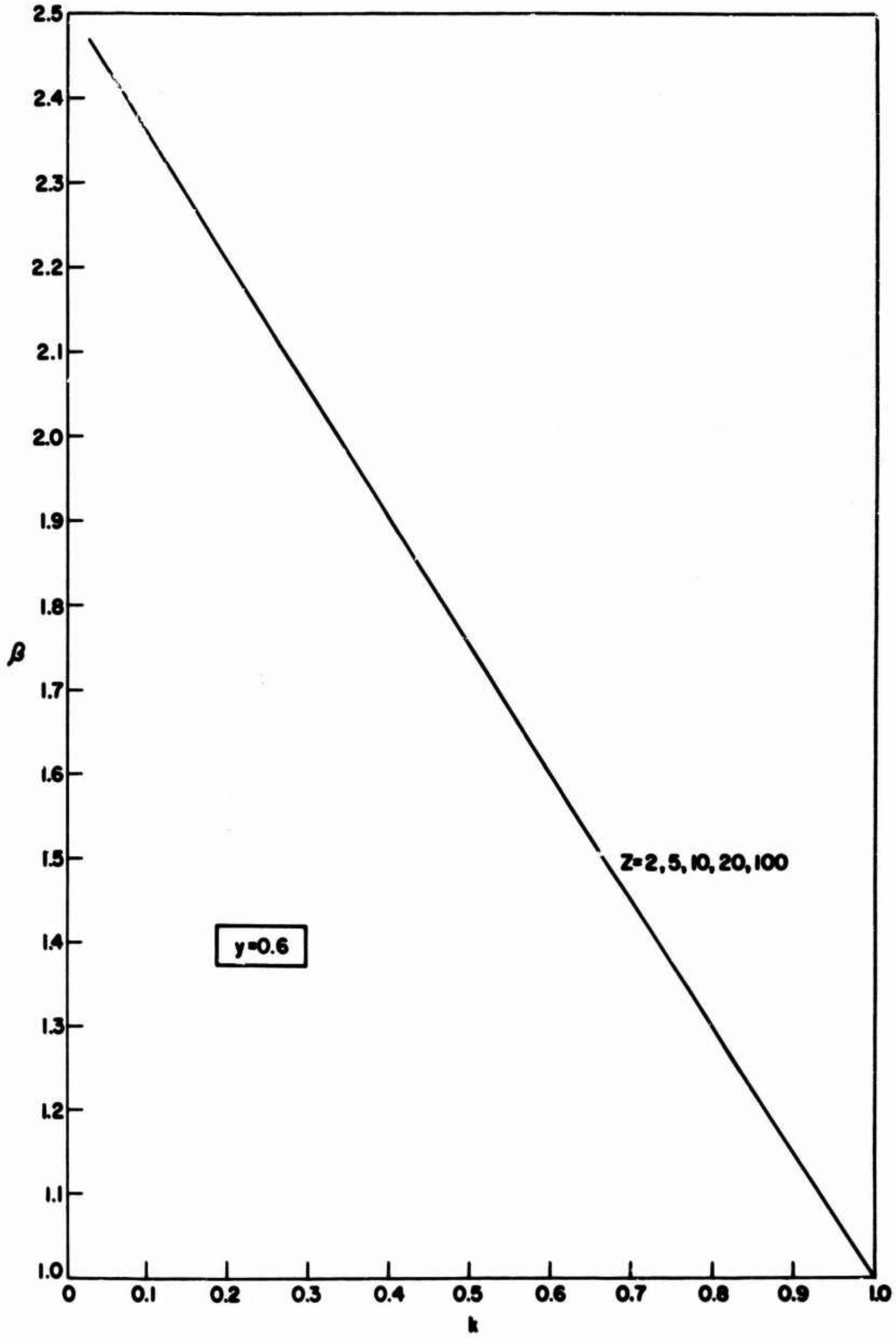

Figure 33. Plot of β vs k when Eq. (42) is Used and k < 1

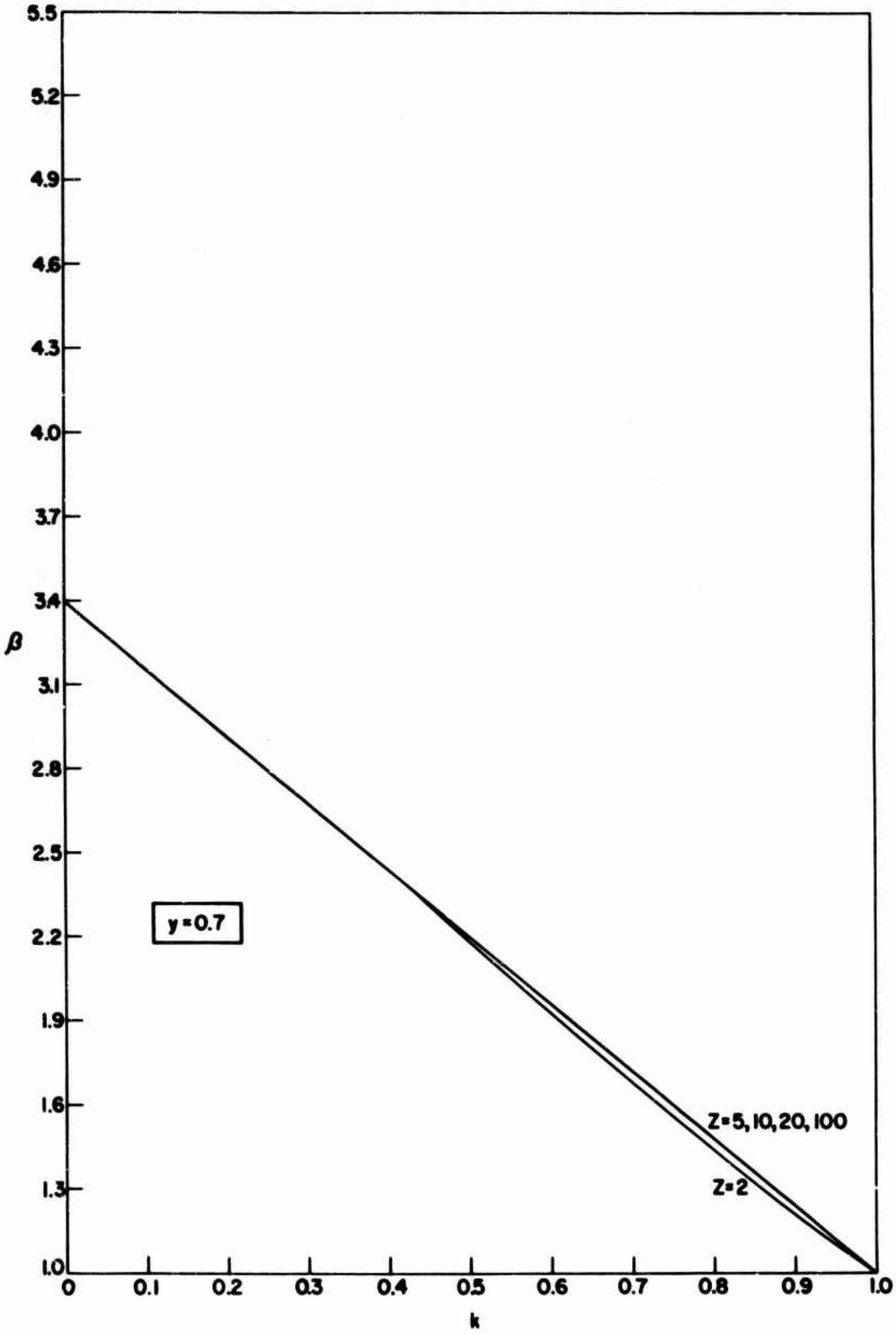

Figure 34. Plot of β vs k when Eq. (42) is Used and k < 1

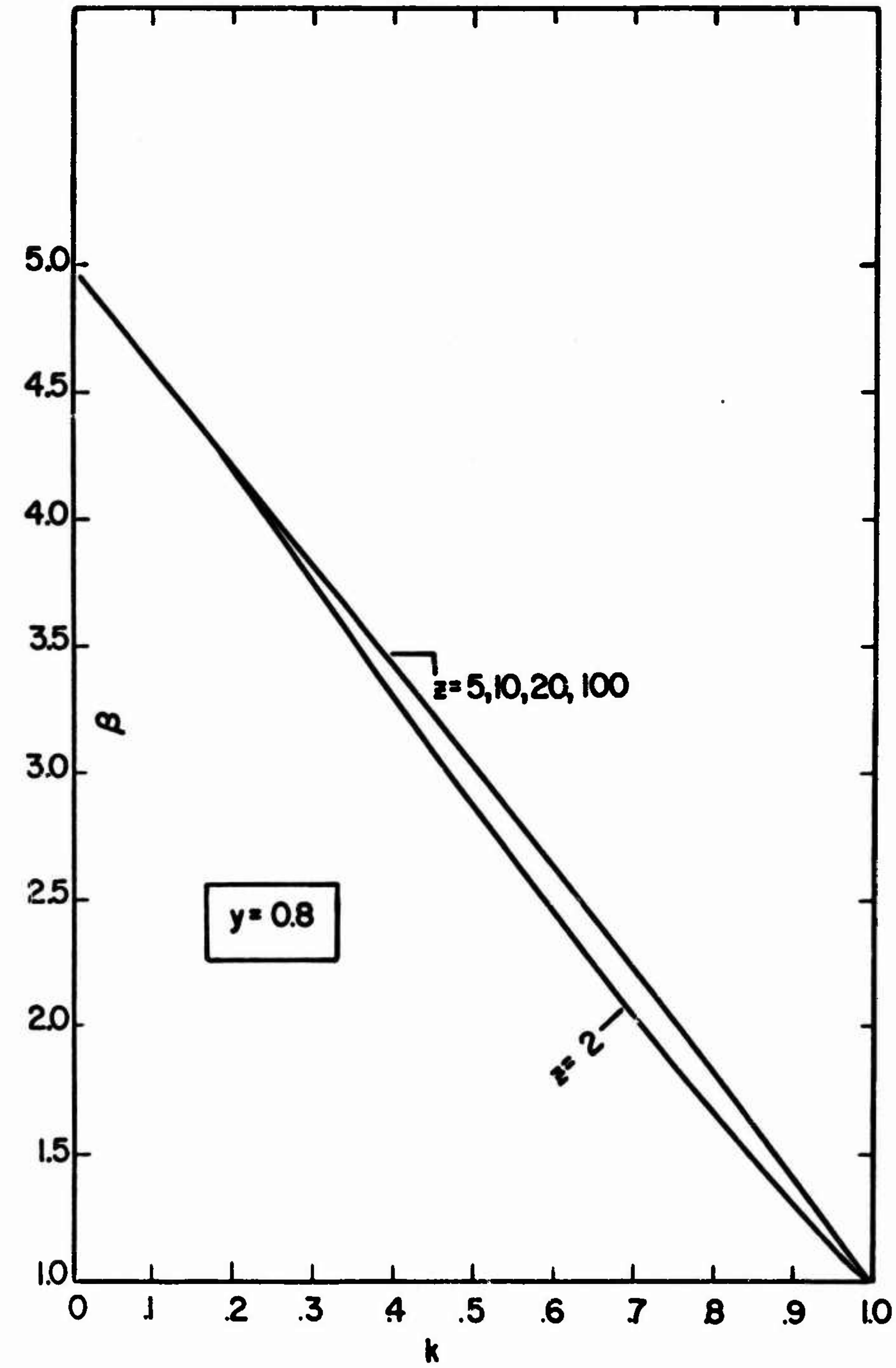

Figure 35. Plot of β vs k when Eq. (42) is Used and k < 1

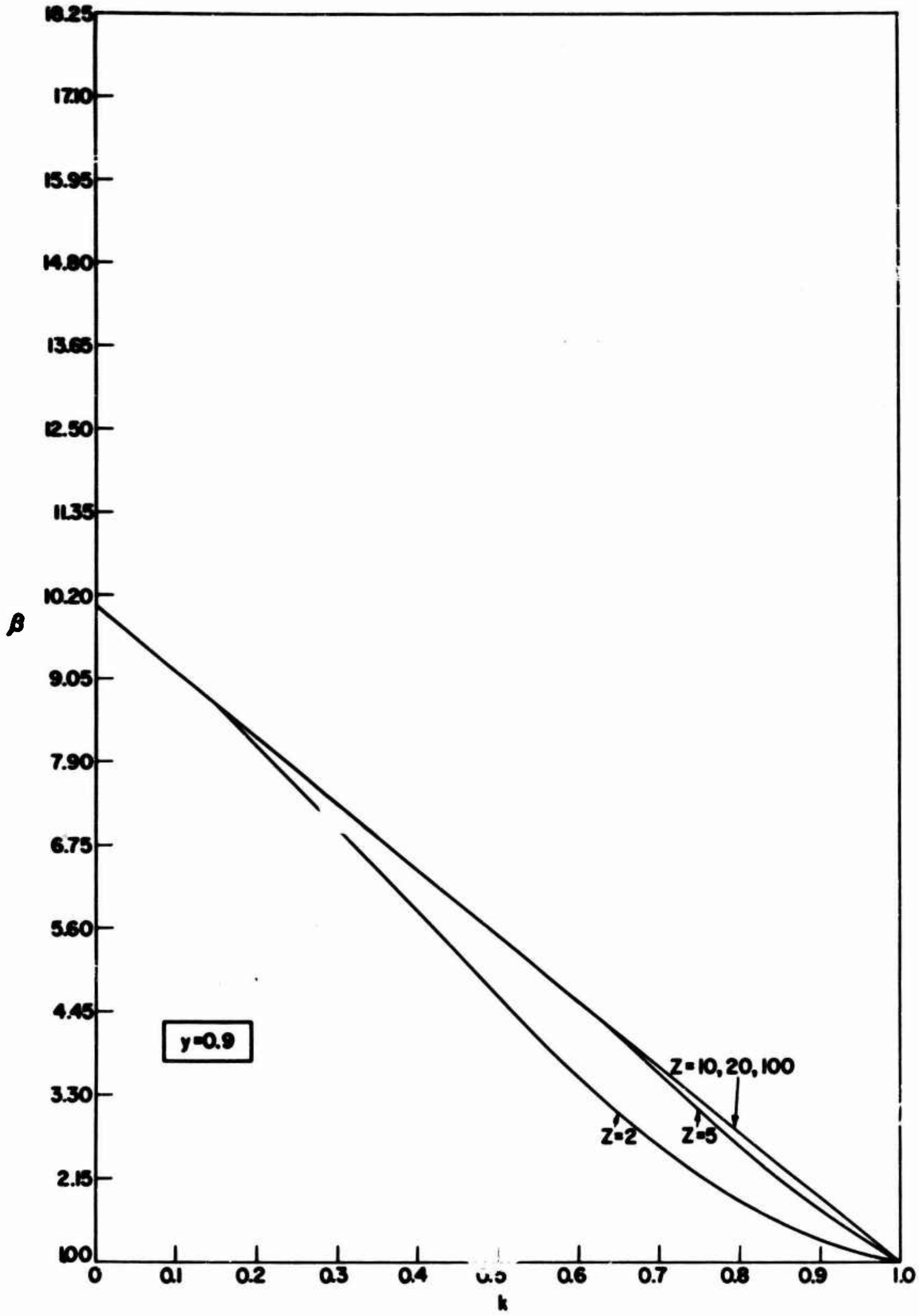

Figure 36. Plot of β vs k when Eq. (42) is Used and $k < 1$

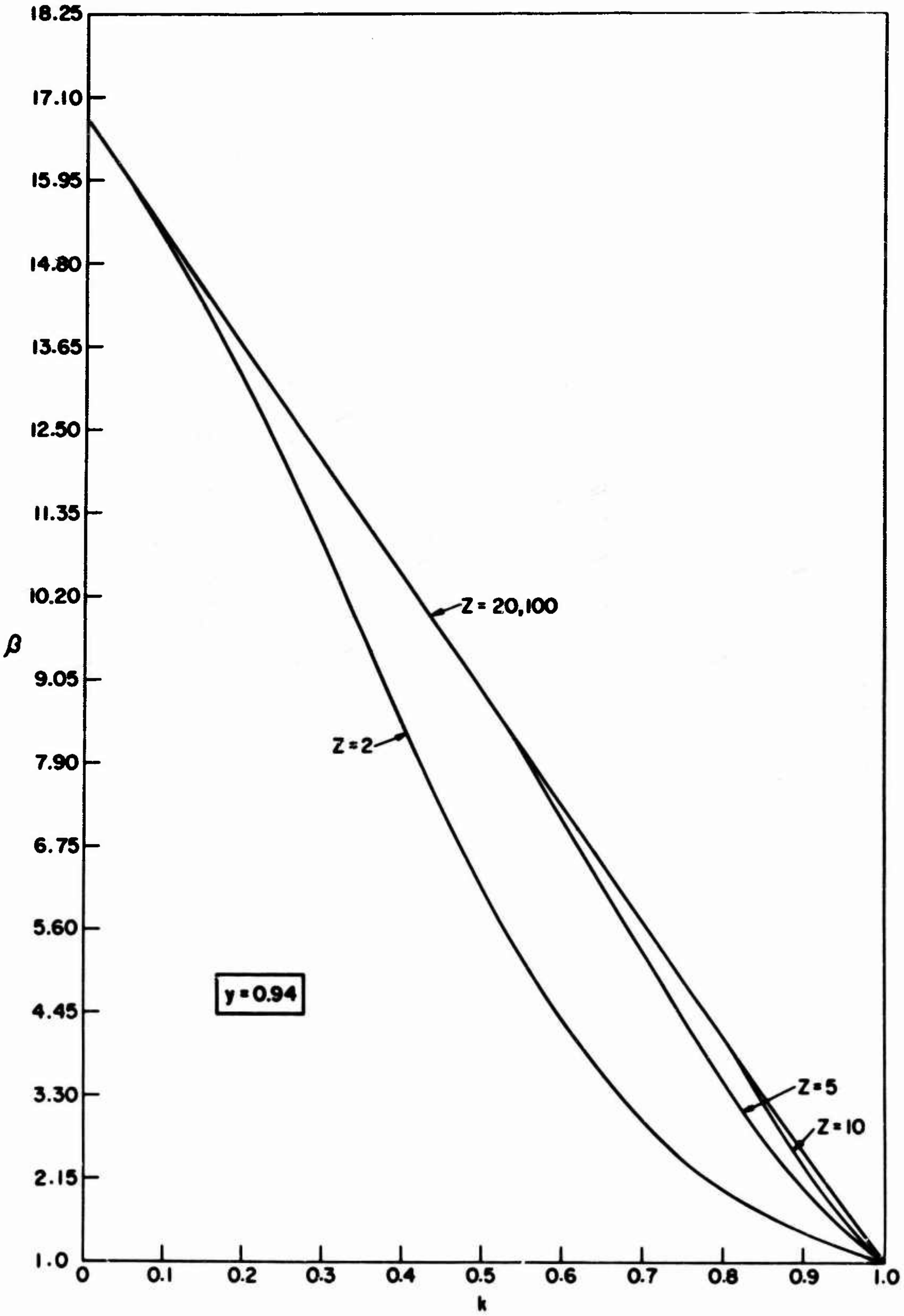

Figure 37. Plot of β vs k when Eq. (42) is Used and k < 1

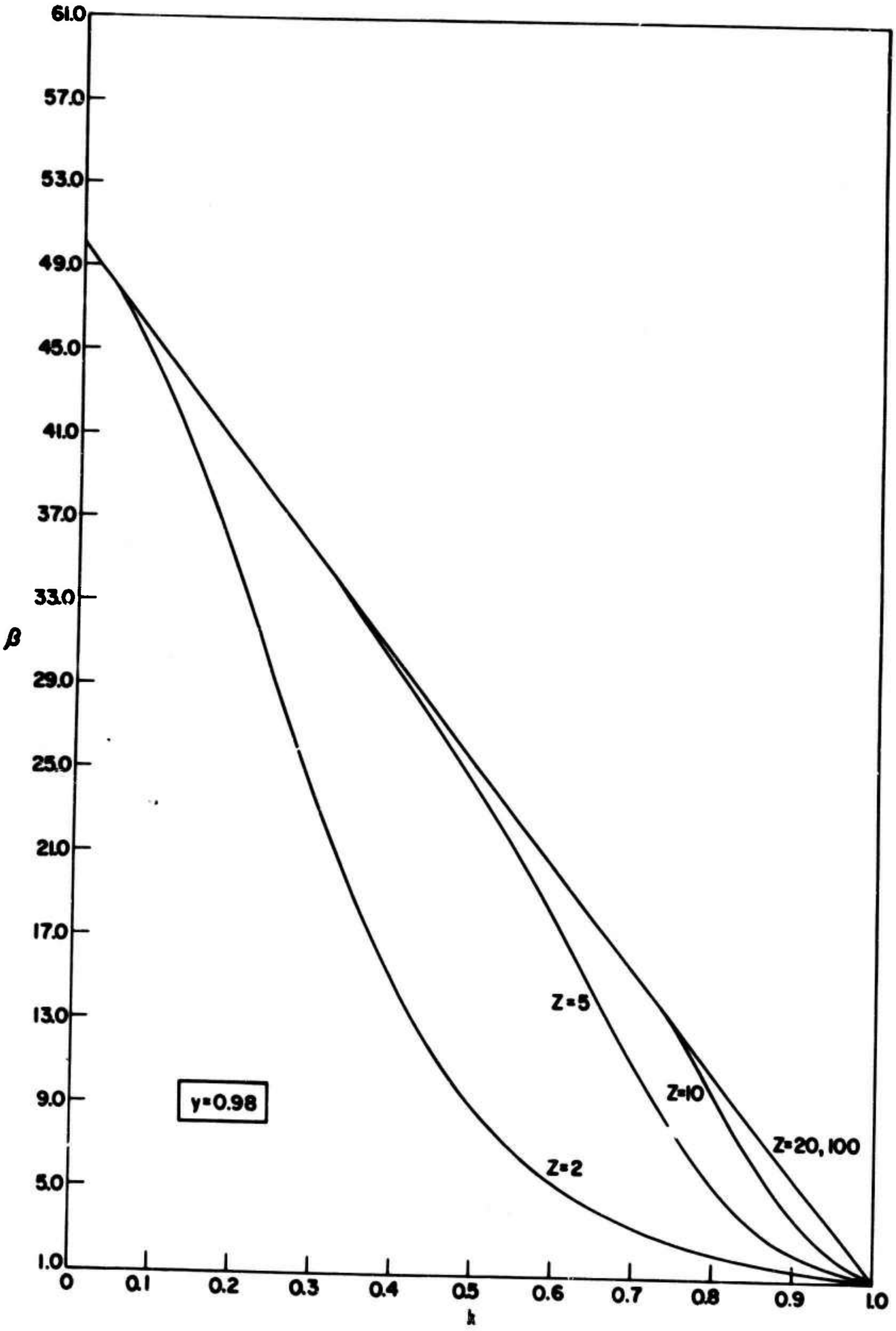

Figure 38. Plot of β vs k when Eq. (42) is Used and k < 1

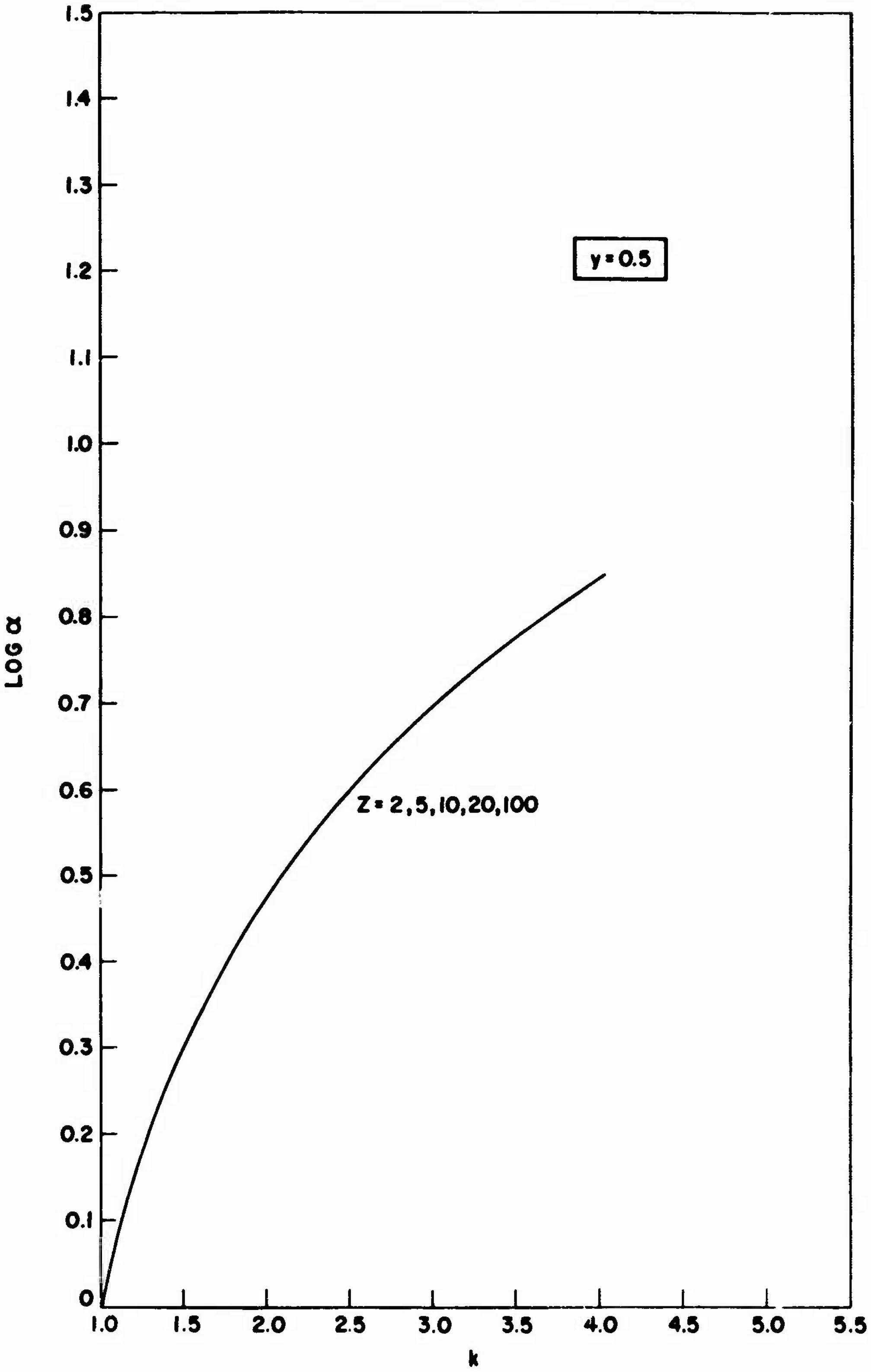

Figure 39. Plot of log α vs k when Eq. (38) is Used and $k > 1$

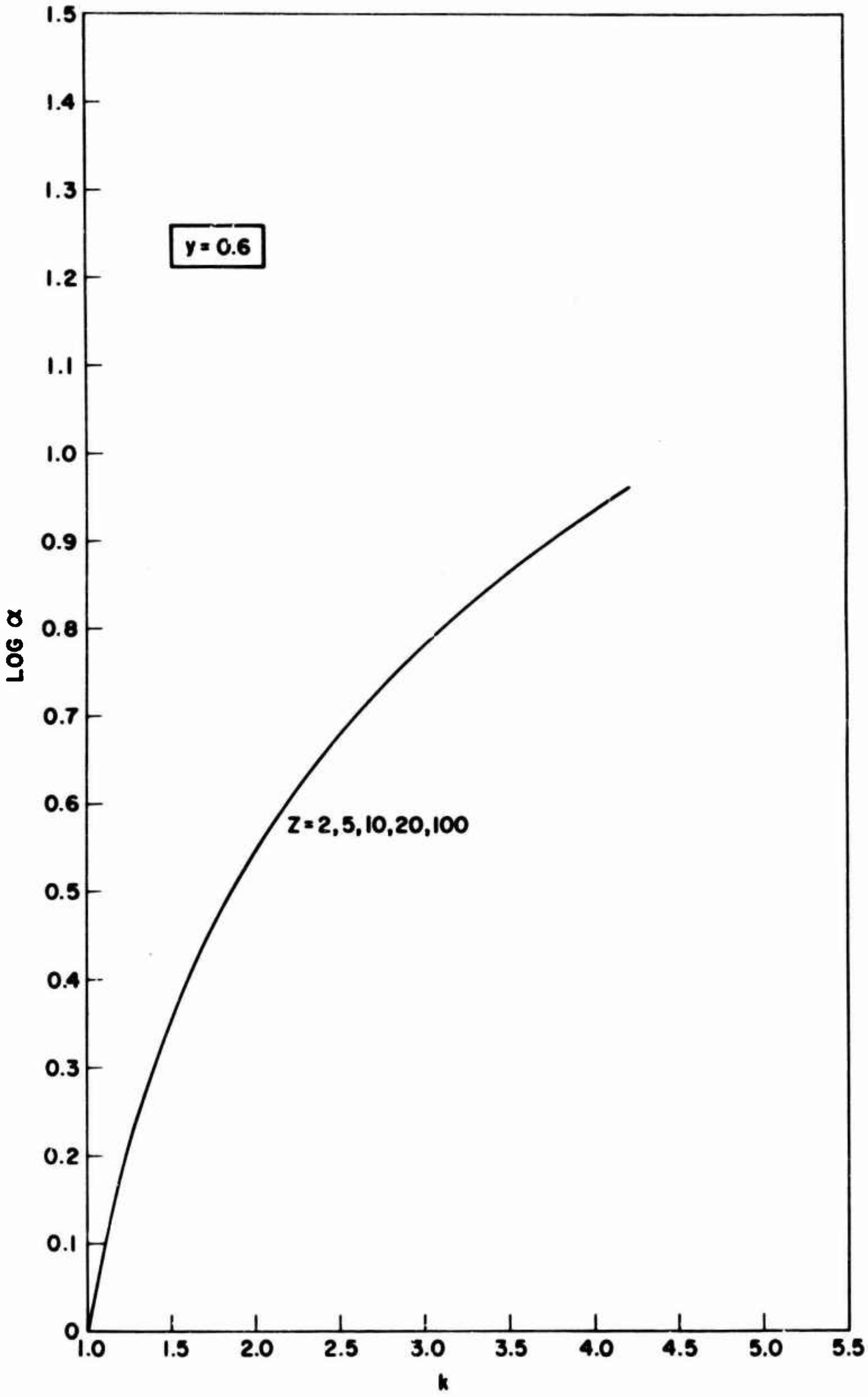

Figure 40. Plot of log α vs k when Eq. (38) is Used and $k > 1$

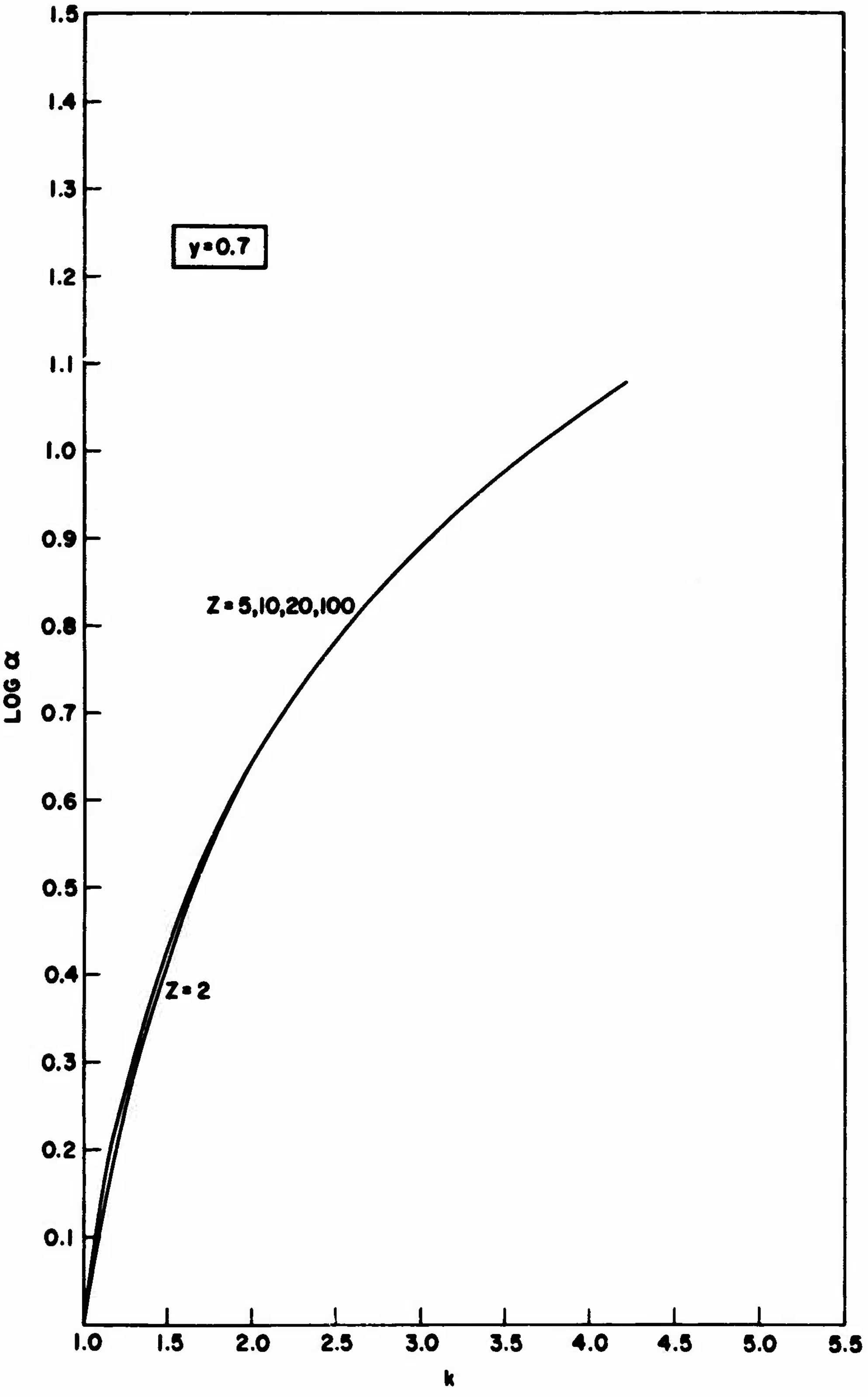

Figure 41. Plot of log α vs k when Eq. (38) is Used and k > 1

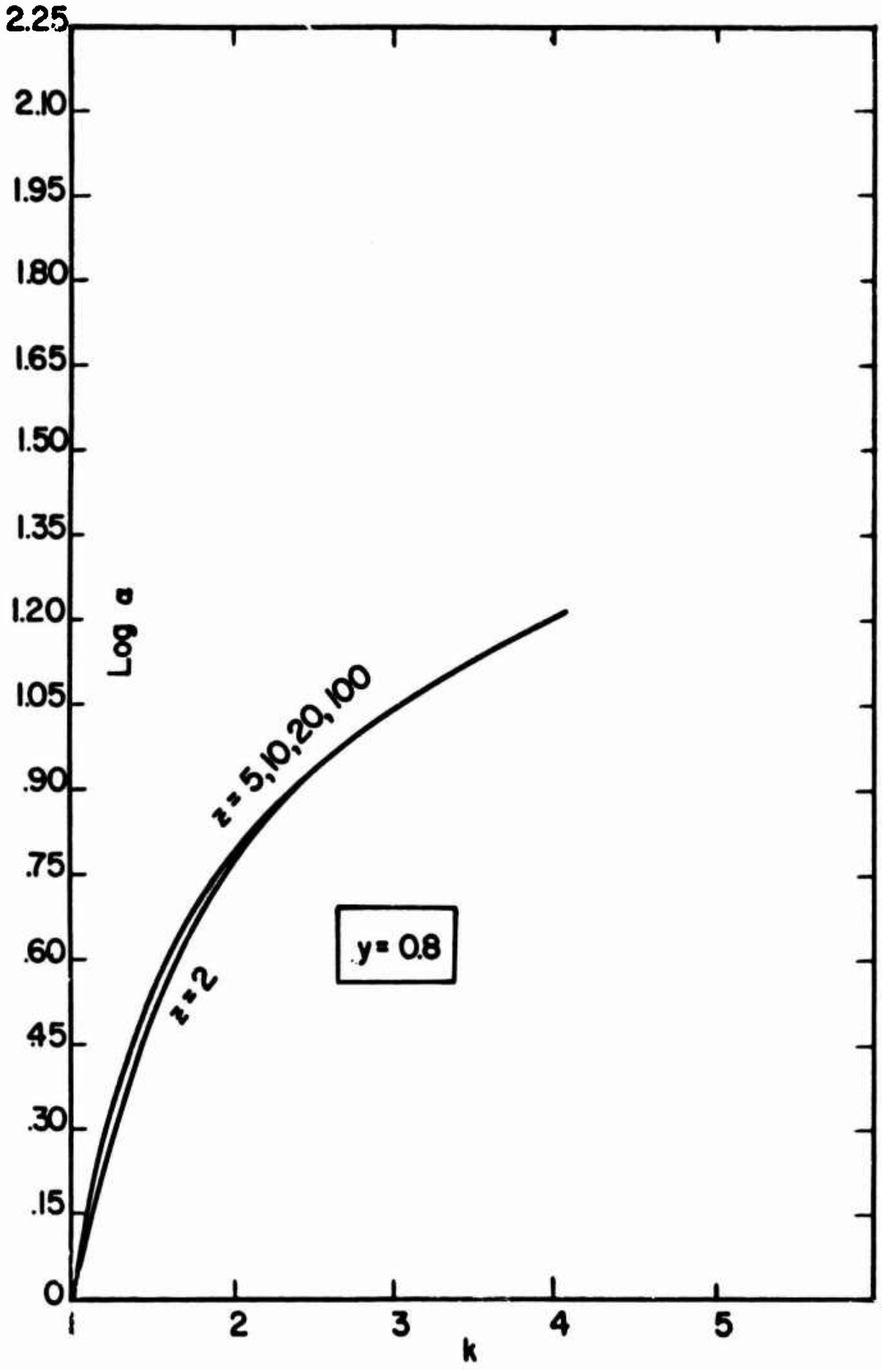

Figure 42. Plot of log a vs k when Eq. (38) is Used and k > 1

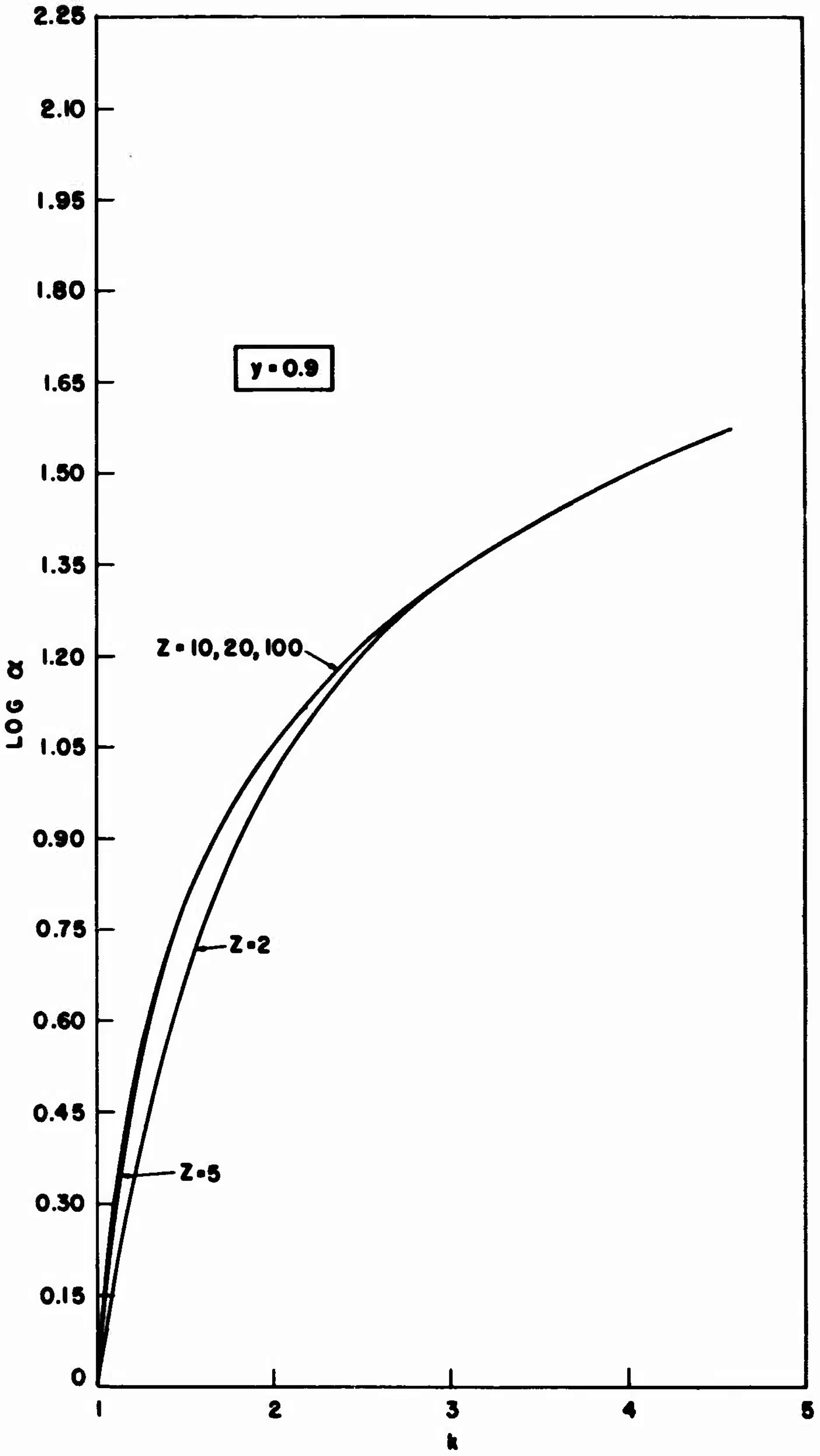

Figure 43. Plot of log α vs k when Eq. (38) is Used and k > 1

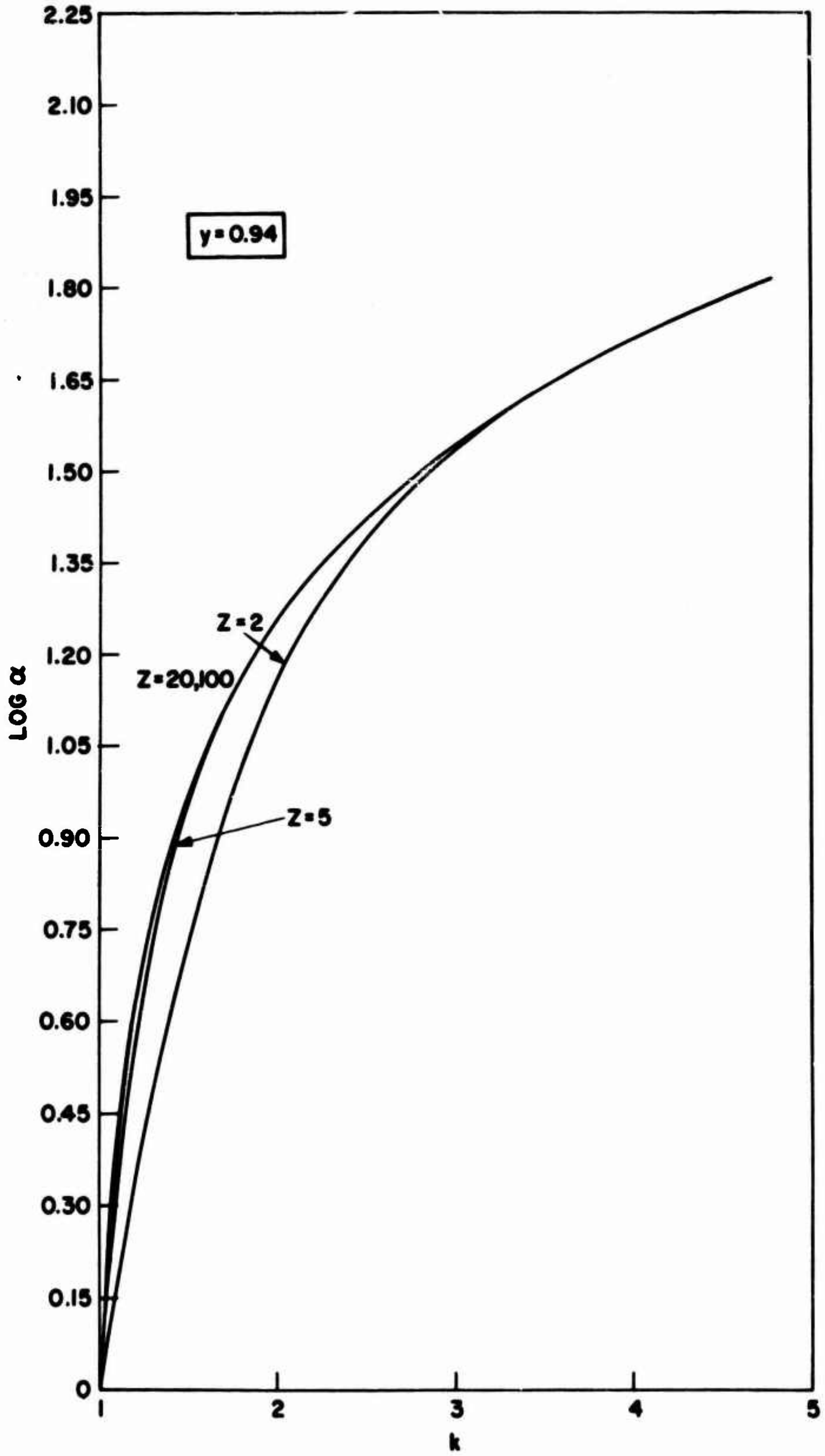

Figure 44. Plot of log α vs k when Eq. (38) is Used and k > 1

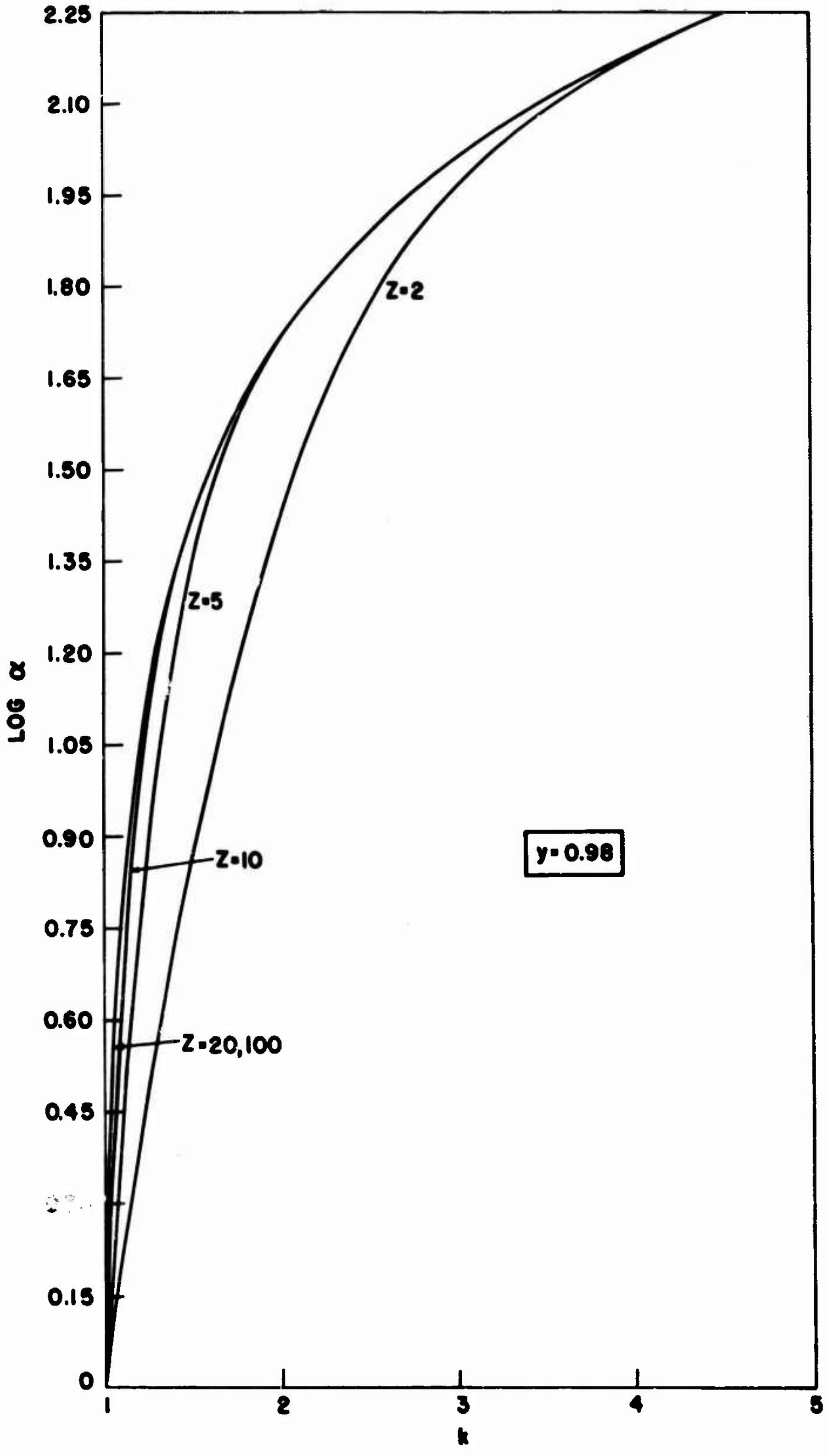

Figure 45. Plot of log α vs k when Eq. (38) is Used and k > 1

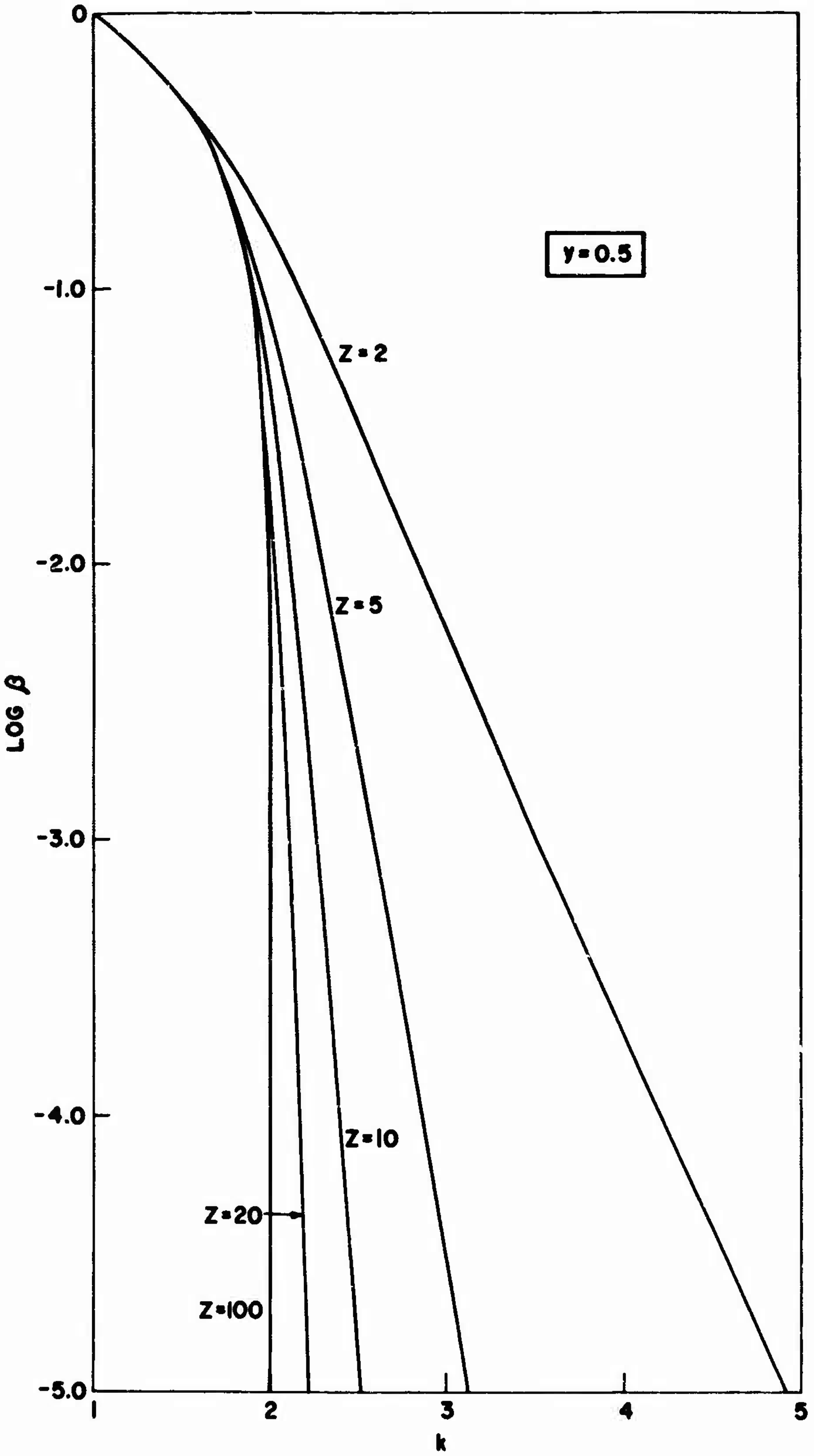

Figure 46. Plot of log β vs k when Eq. (40) is Used and k > 1

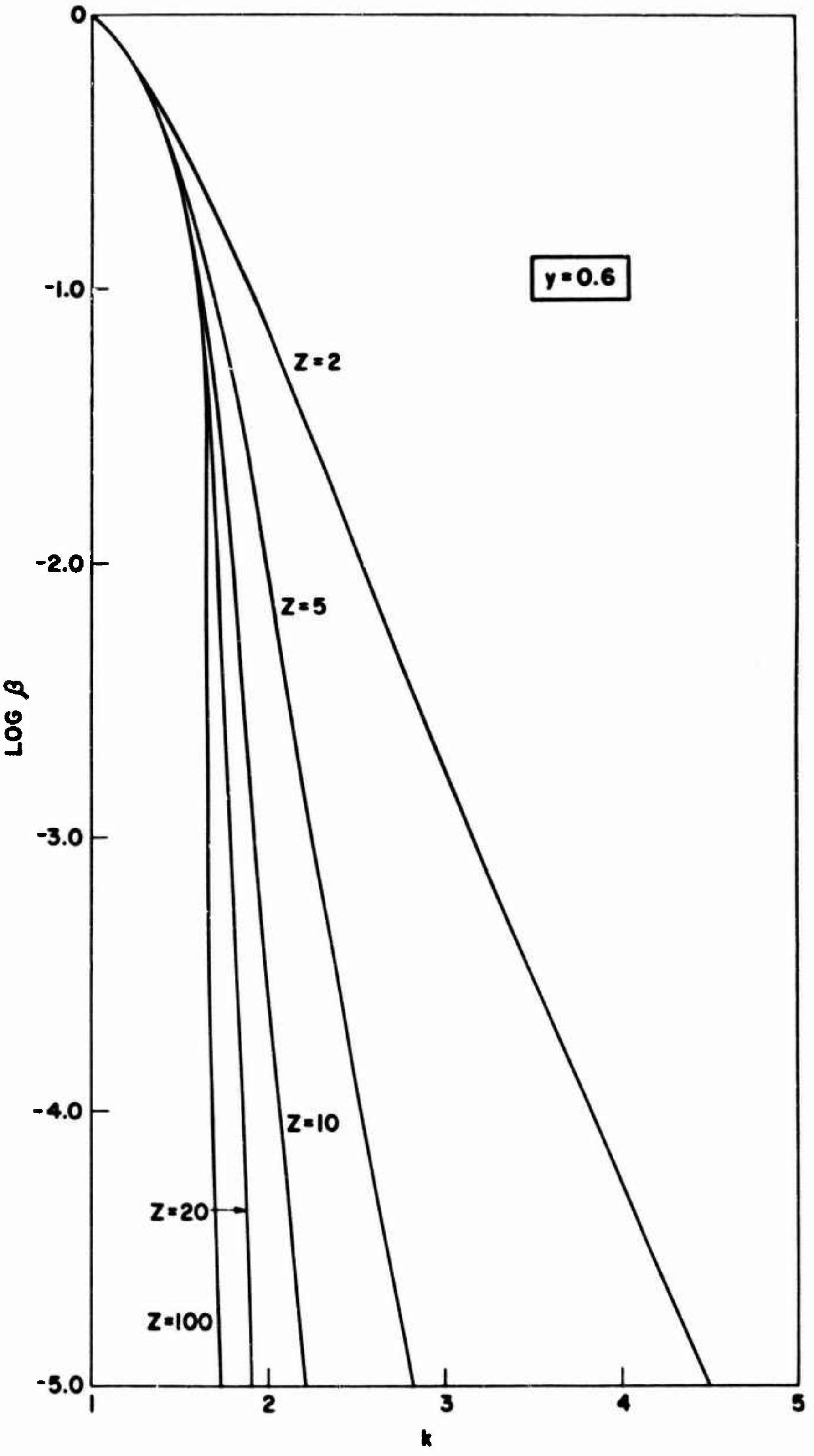

Figure 47. Plot of log β vs k when Eq. (40) is Used and k > 1

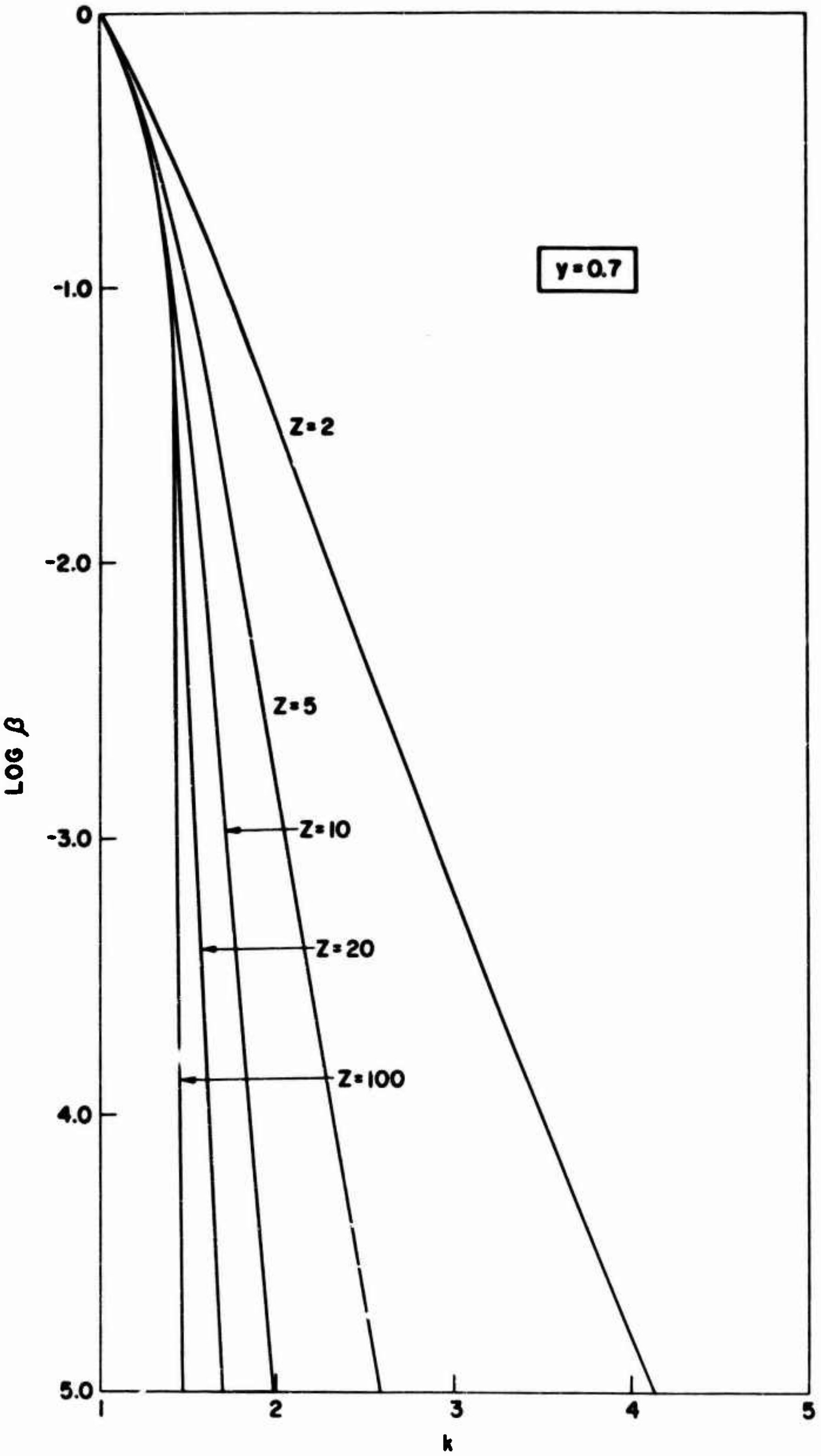

Figure 48. Plot of log β vs k when Eq. (40) is Used and k > 1

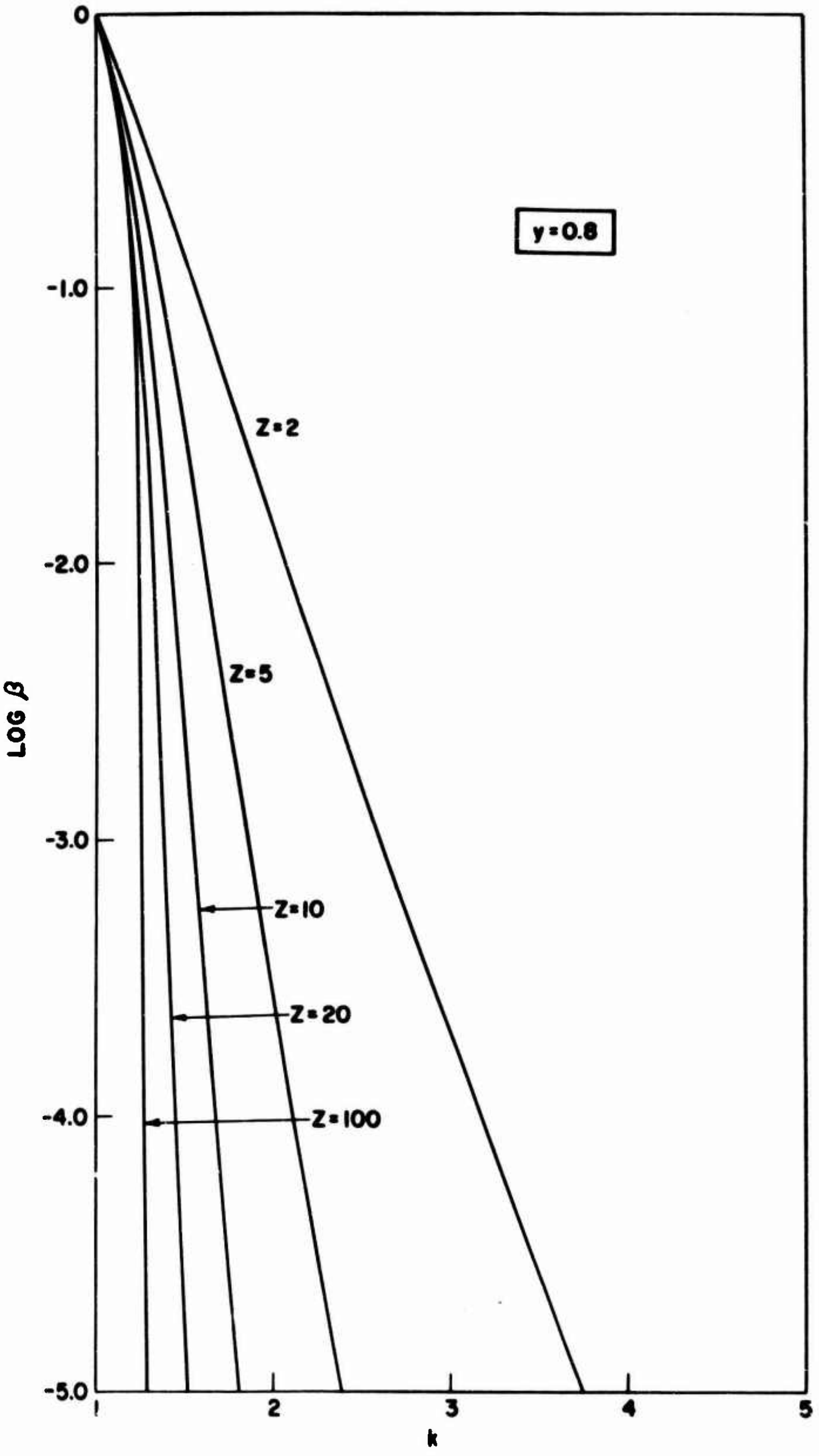

Figure 49. Plot of log β vs k when Eq. (40) is Used and k > 1

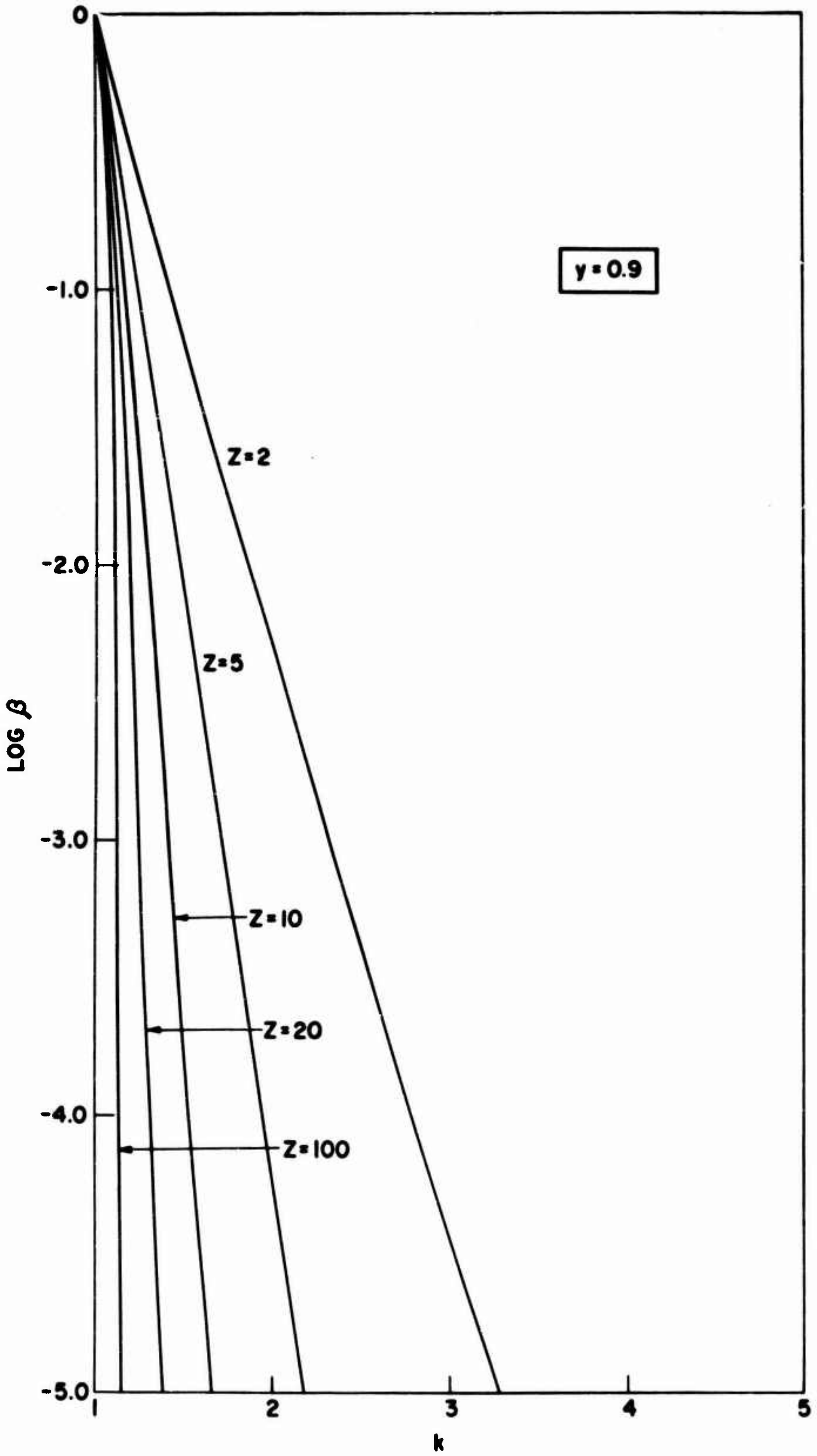

Figure 50. Plot of log β vs k when Eq. (40) is Used and k > 1

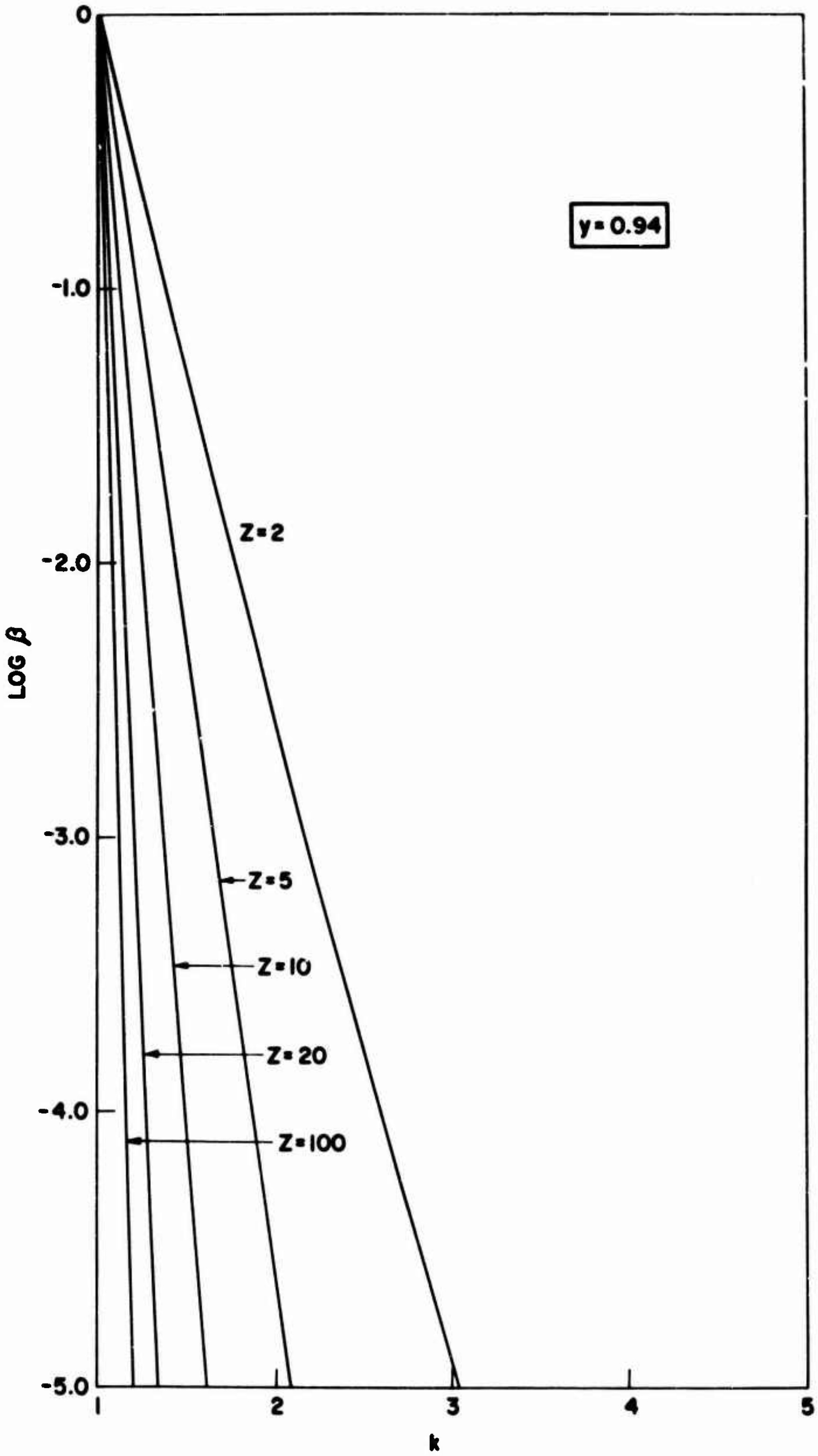

Figure 51. Plot of log β vs k when Eq. (40) is Used and k > 1

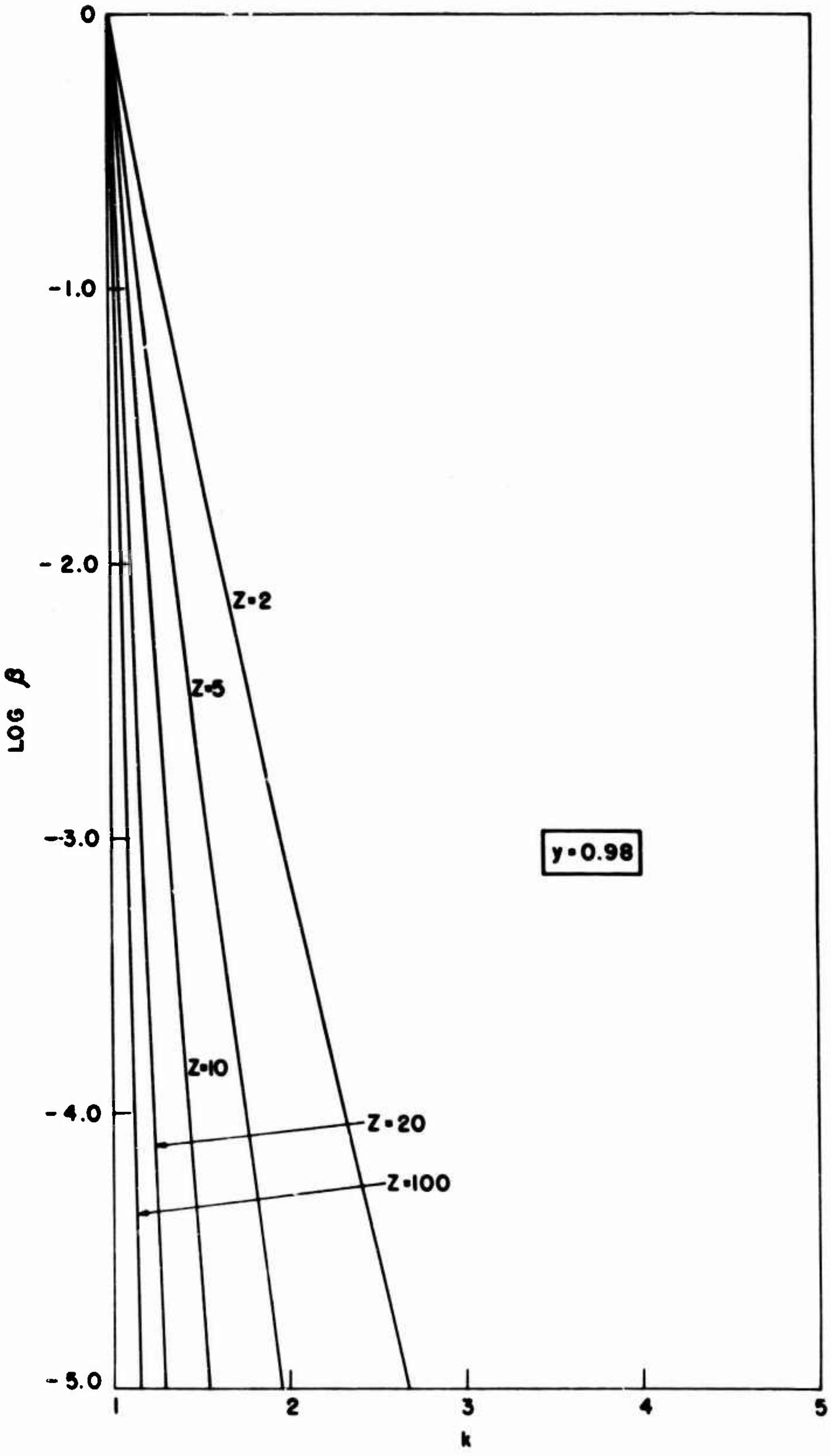

Figure 52. Plot of log β vs k when Eq. (40) is Used and k > 1

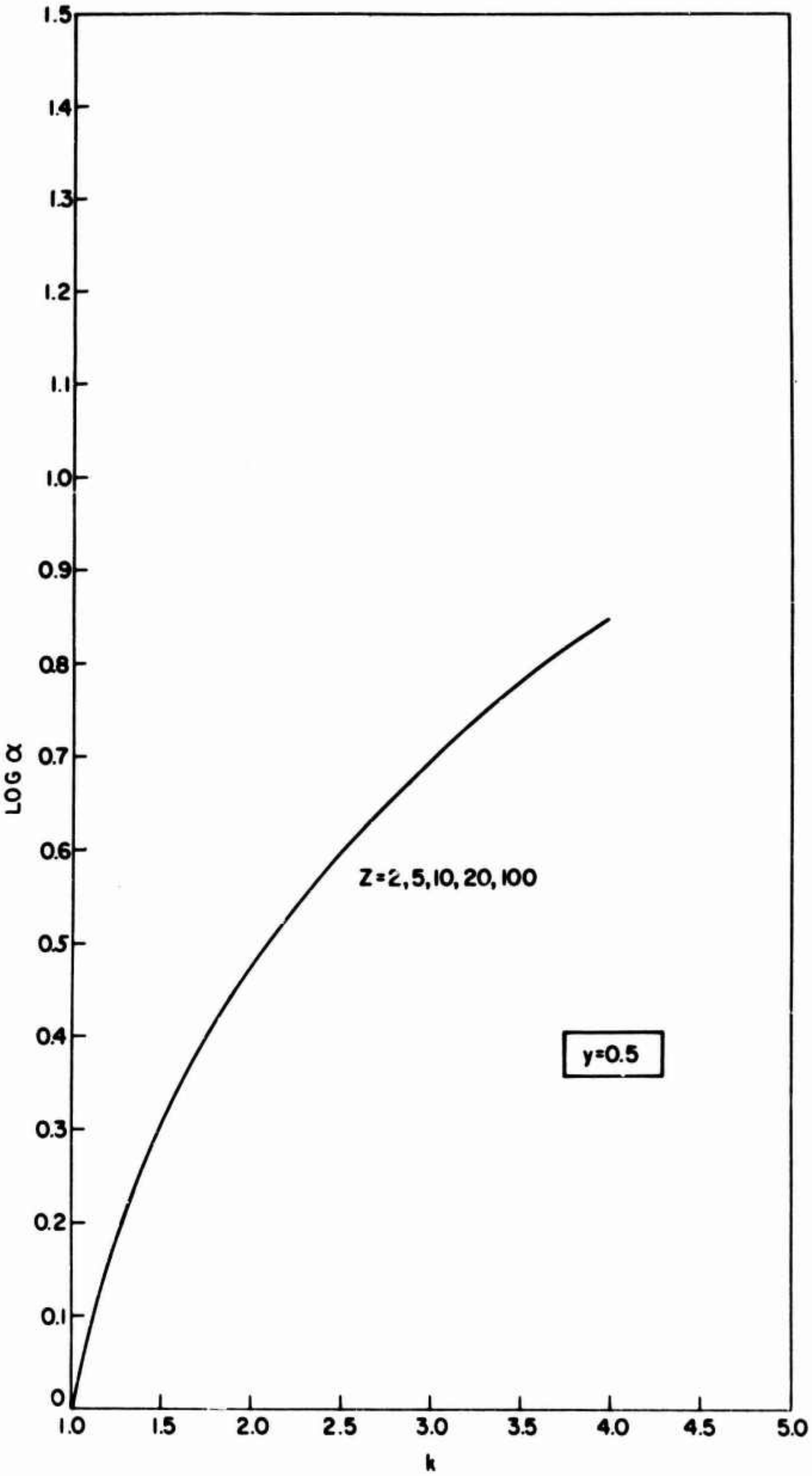

Figure 53. Plot of log α vs k when Eq. (41) is Used and $k > 1$

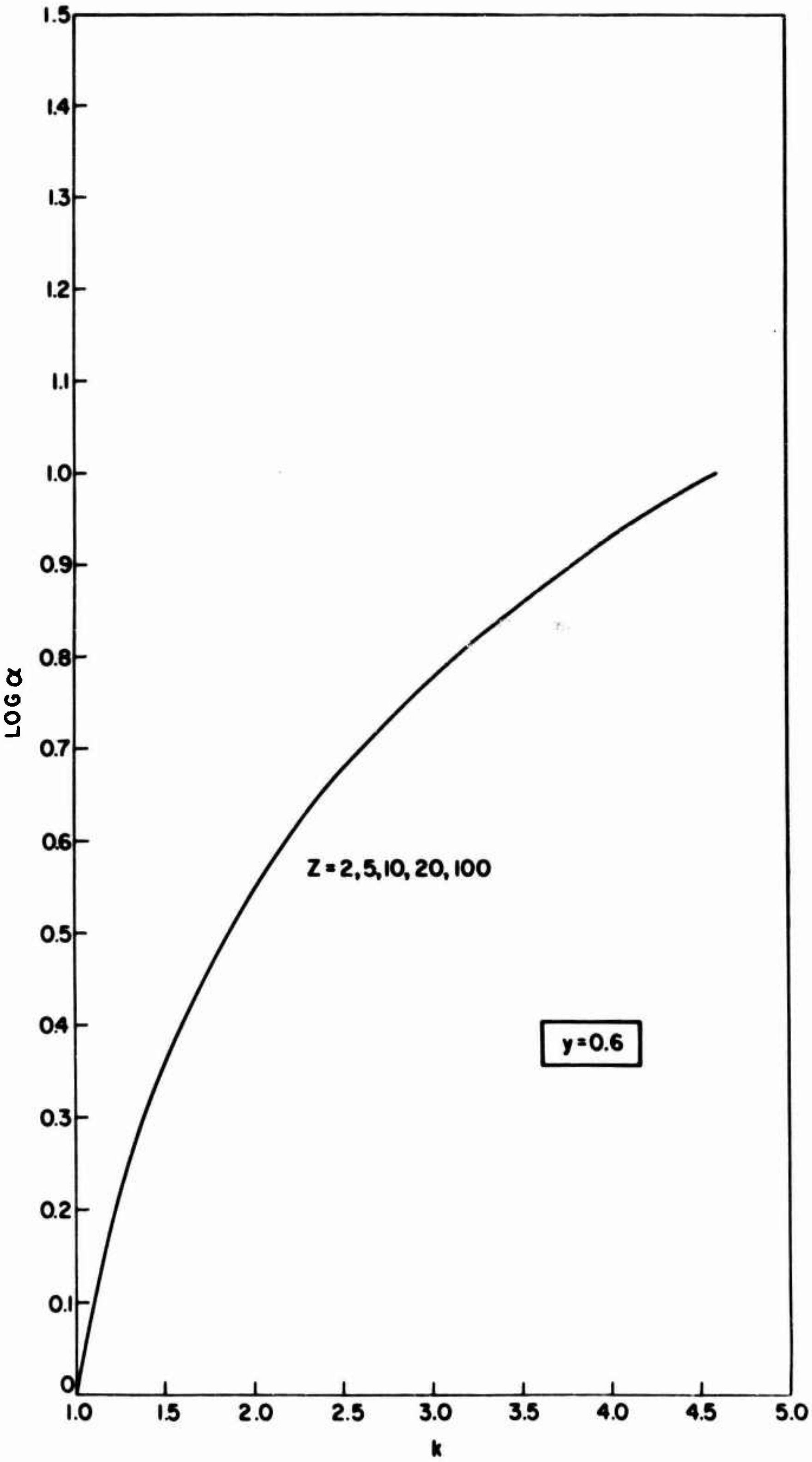

Figure 54. Plot of log α vs k when Eq. (41) is Used and k > 1

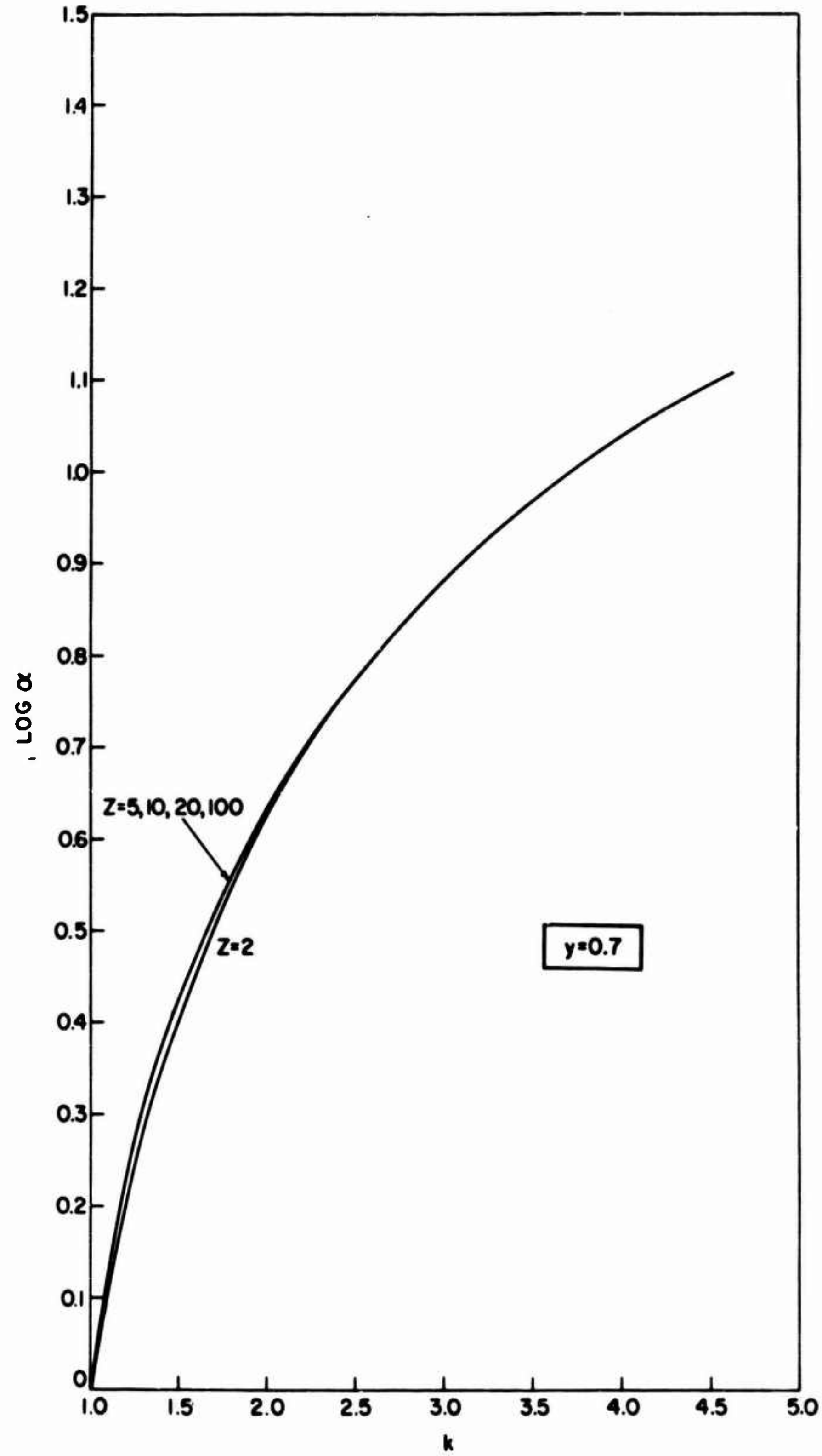

Figure 55. Plot of log α vs k when Eq. (41) is Used and k > 1

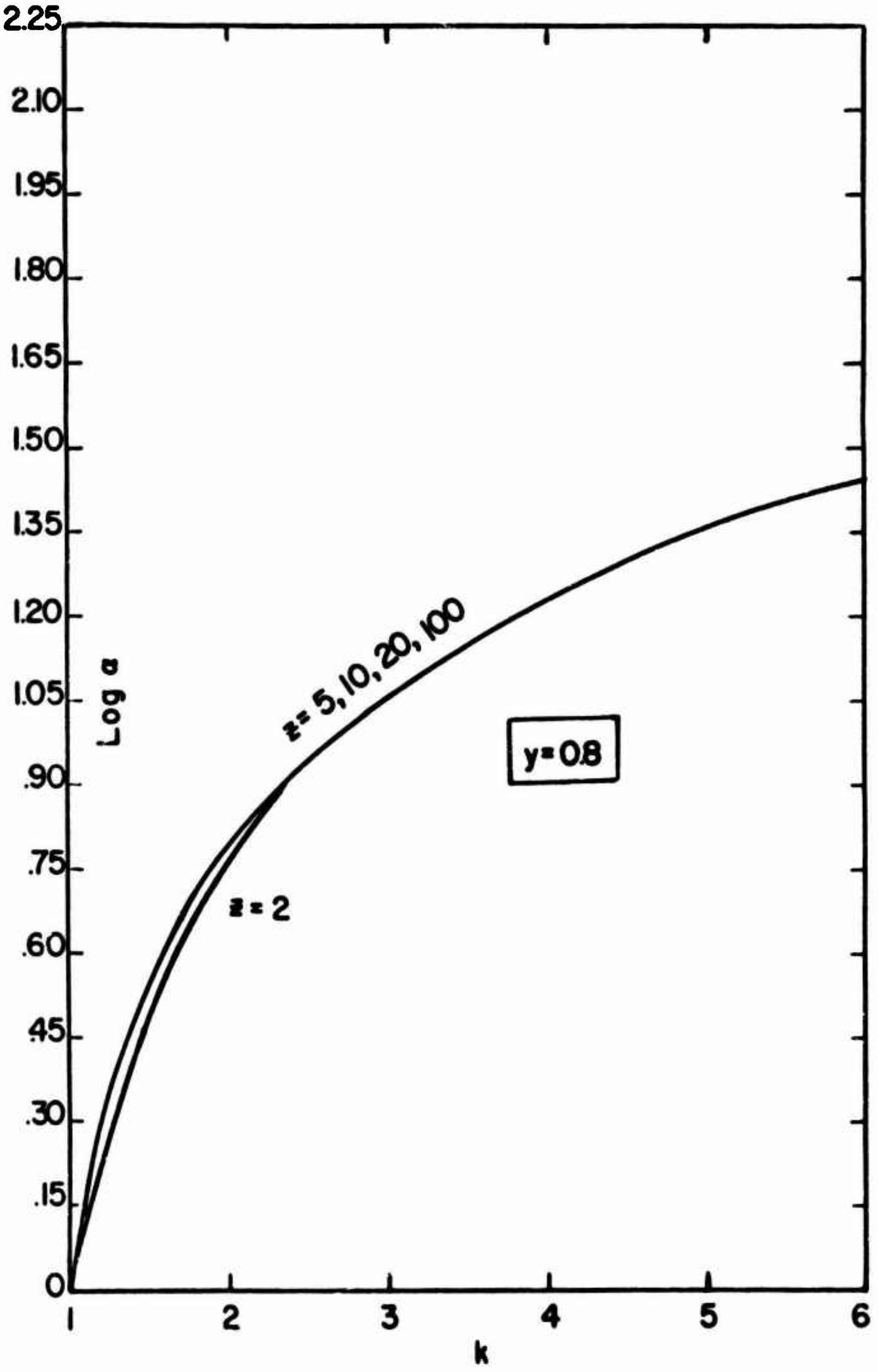

Figure 56. Plot of log a vs k when Eq. (41) is Used and k > 1

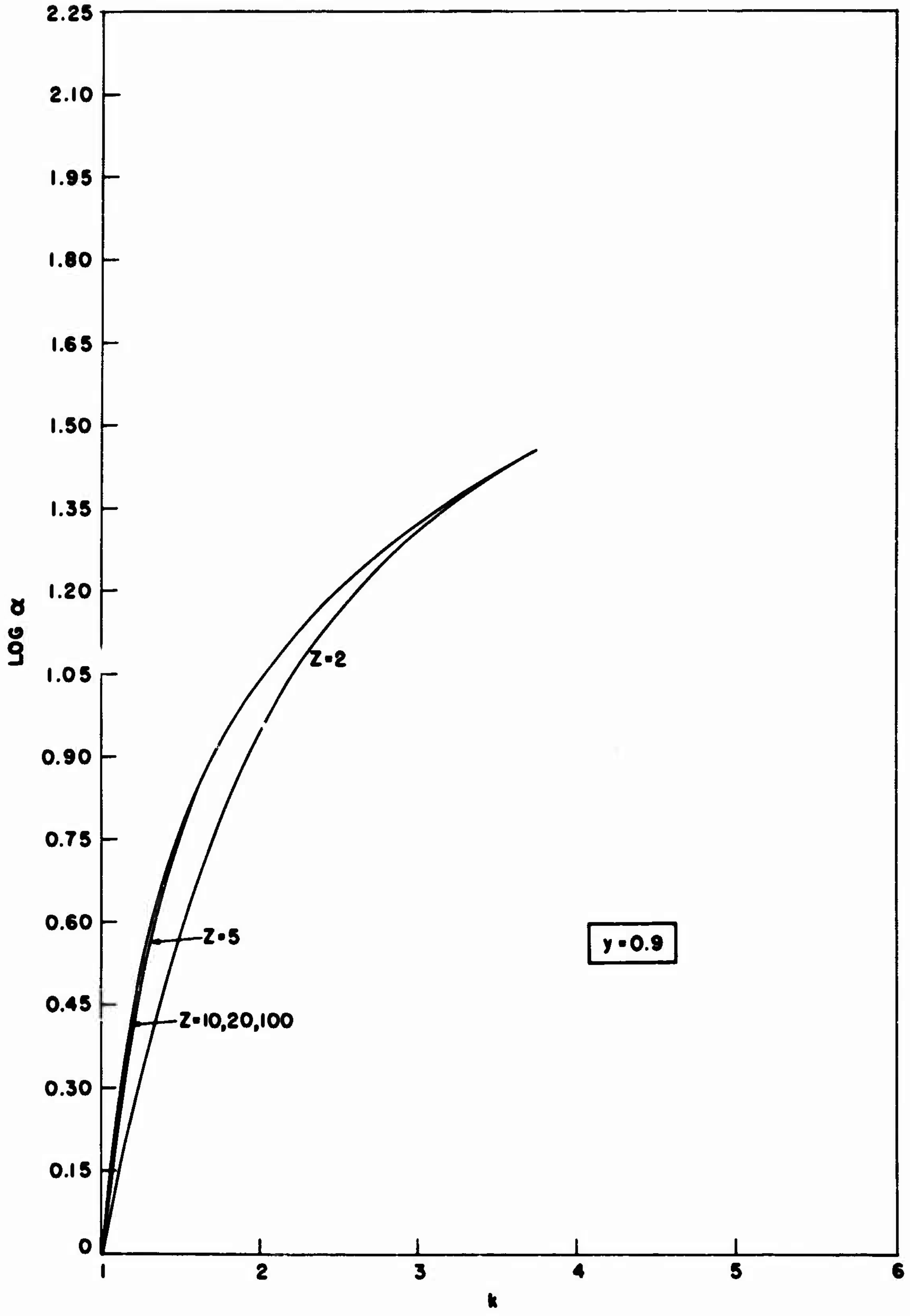

Figure 57. Plot of log α vs k when Eq. (41) is Used and k > 1

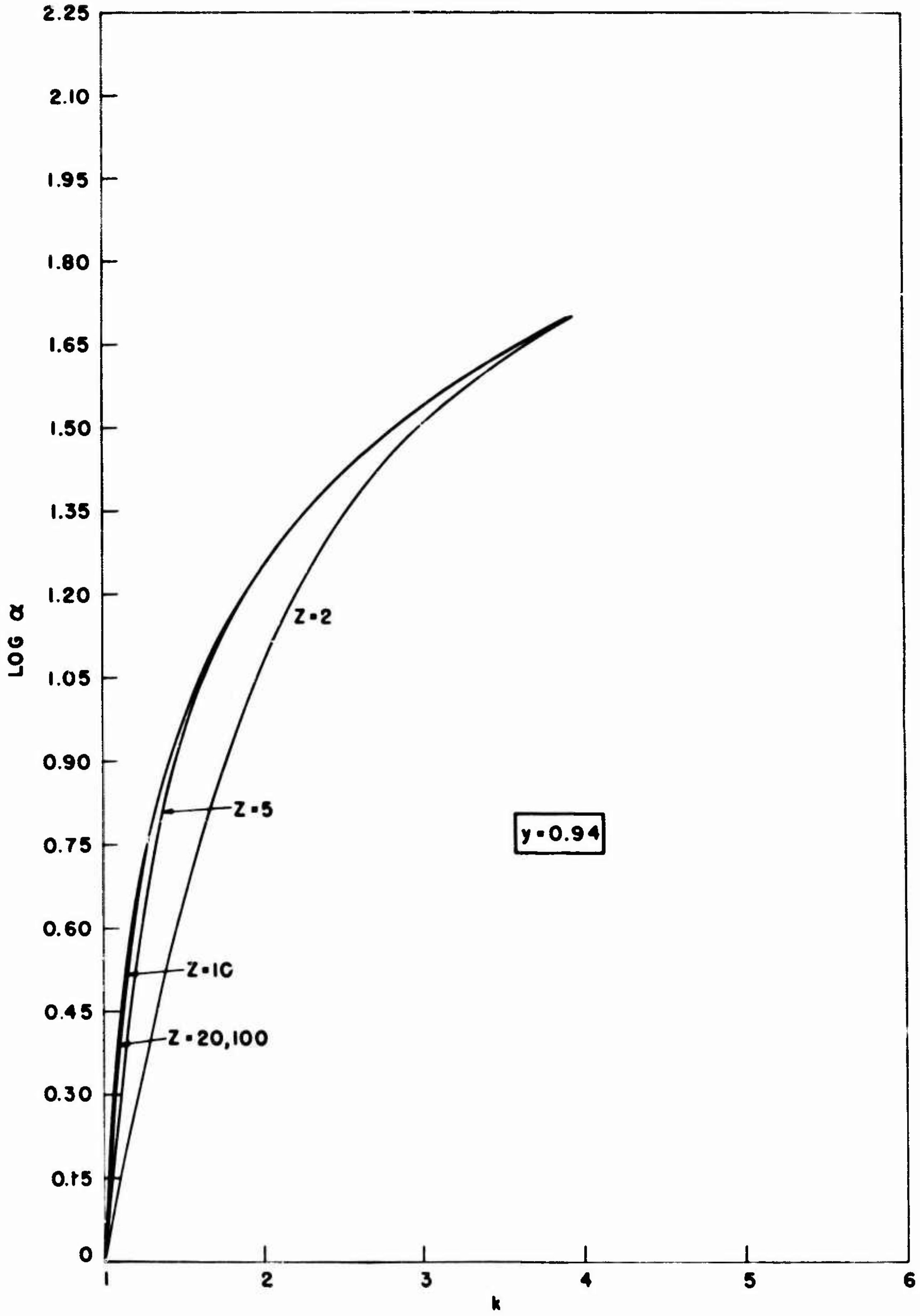

Figure 58. Plot of log α vs k when Eq. (41) is Used and k > 1

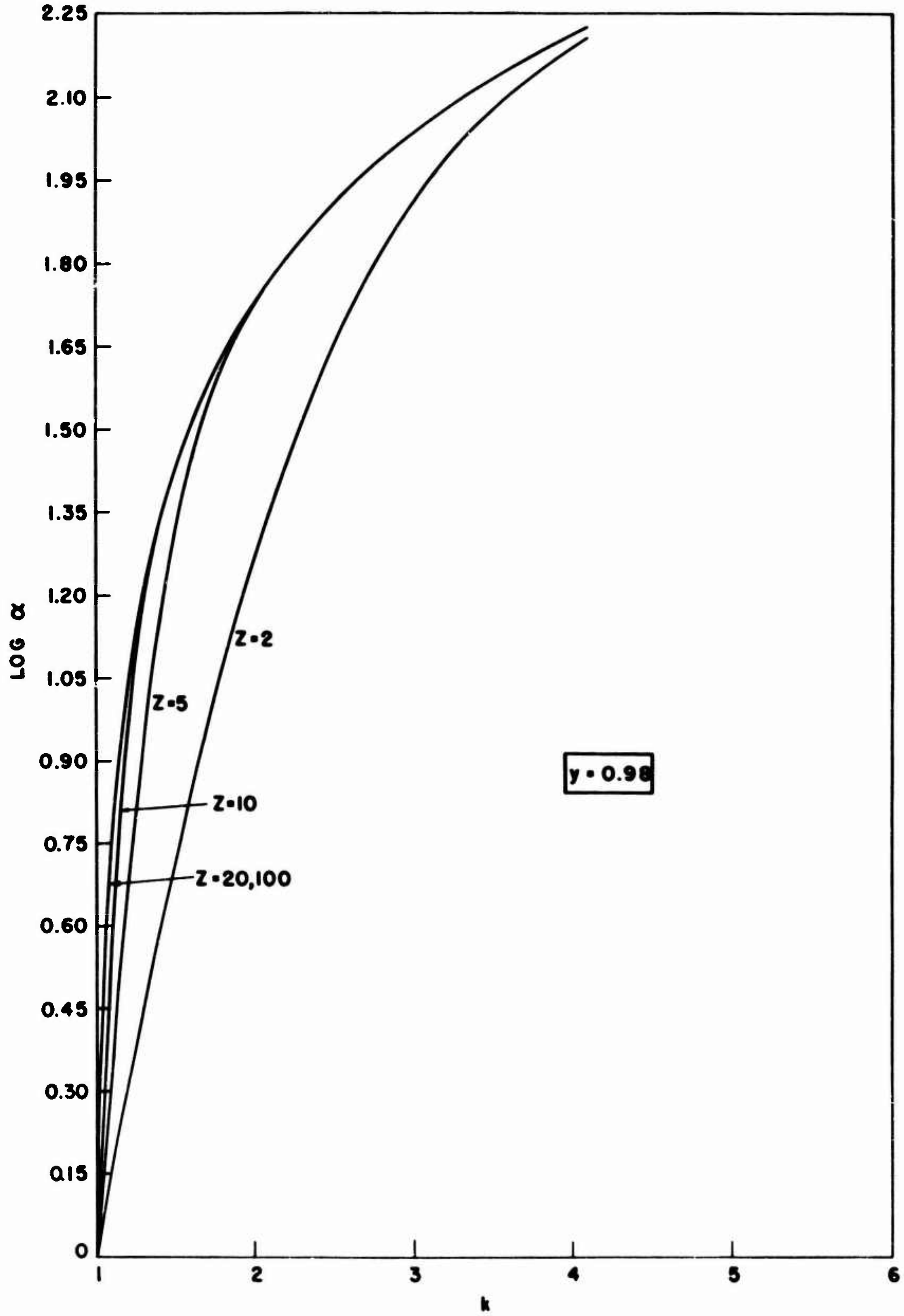

Figure 59. Plot of log α vs k when Eq. (41) is Used and k > 1

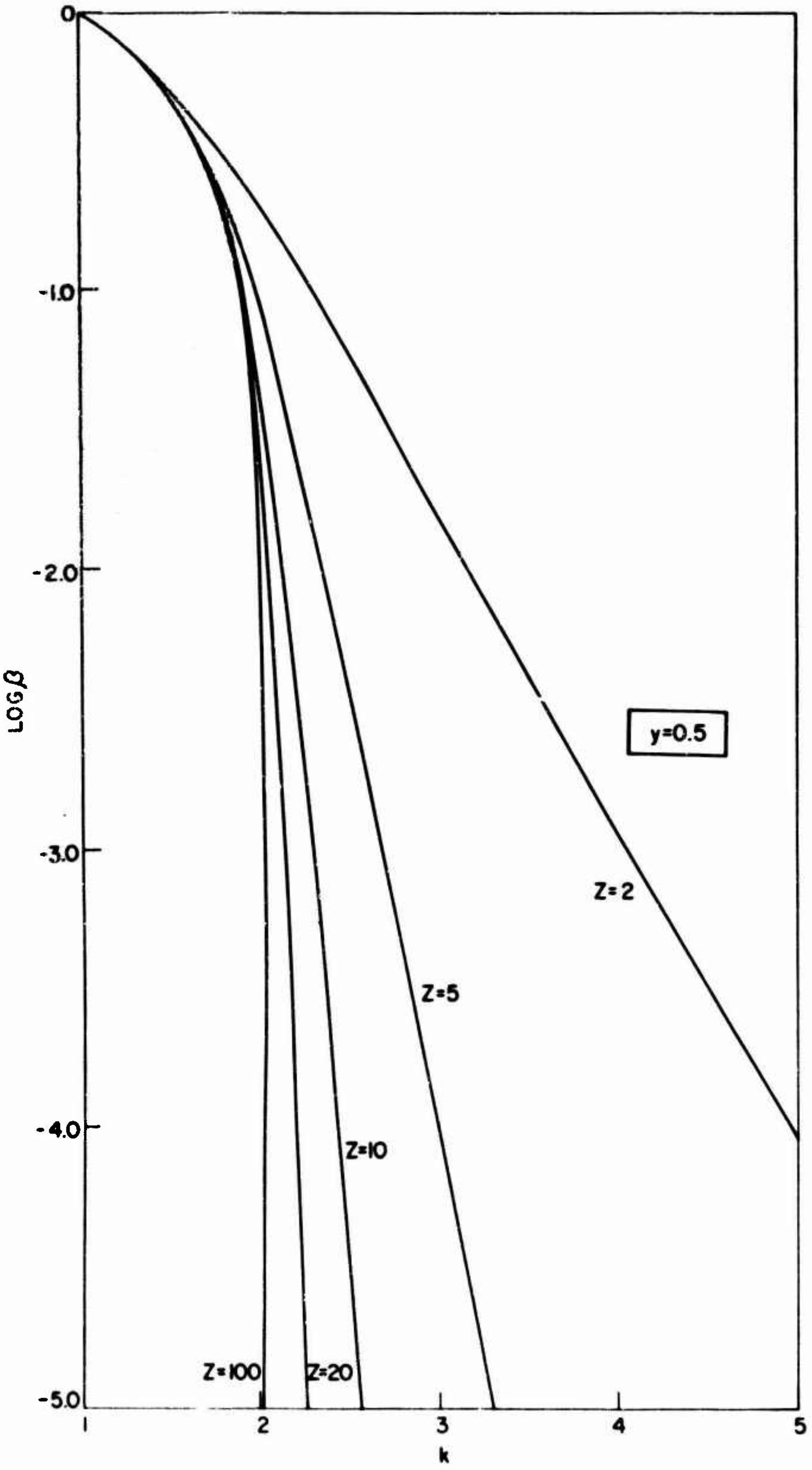

Figure 60. Plot of log β vs k when Eq. (42) is Used and k > 1

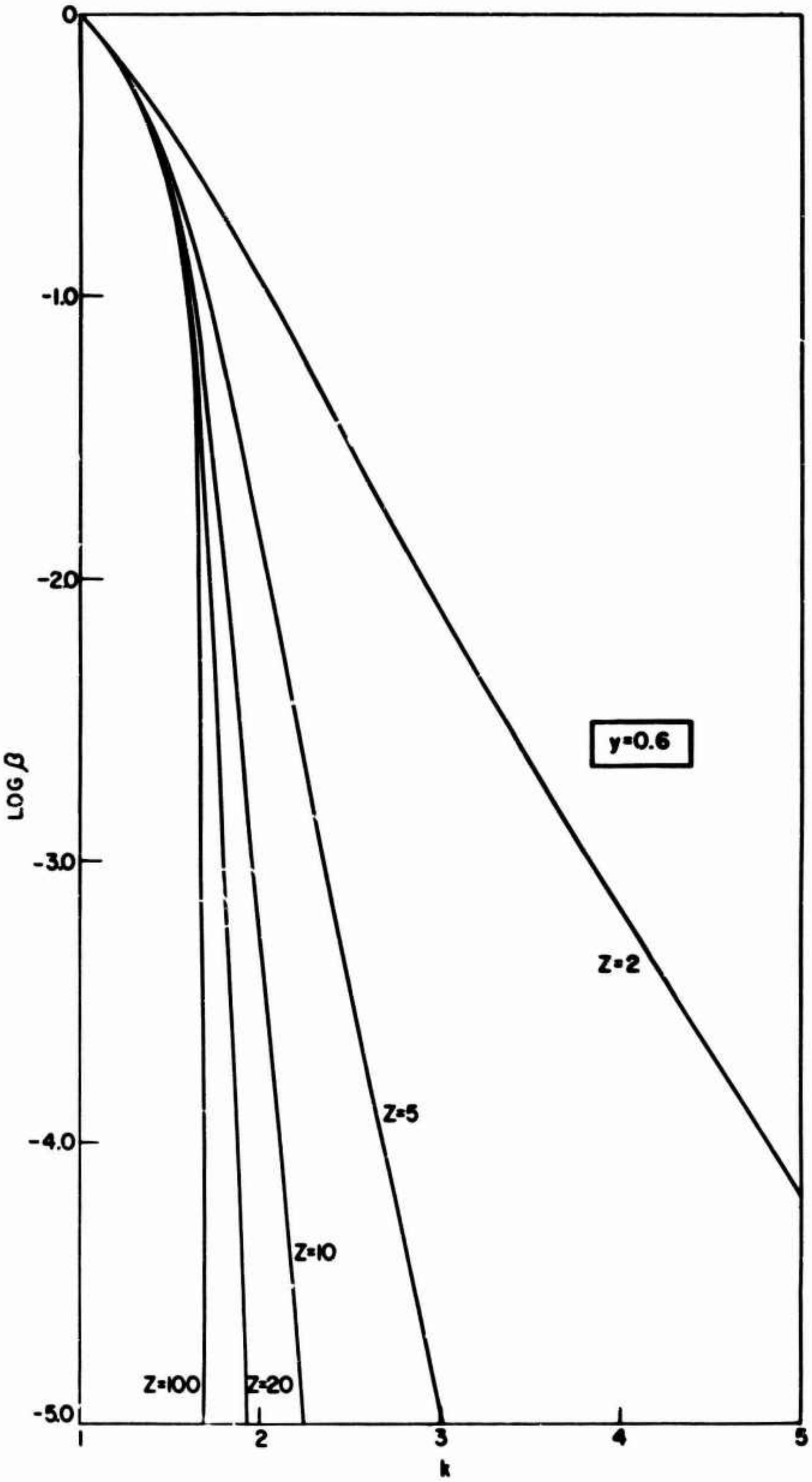

Figure 61. Plot of log β vs k when Eq. (42) is Used and k > 1

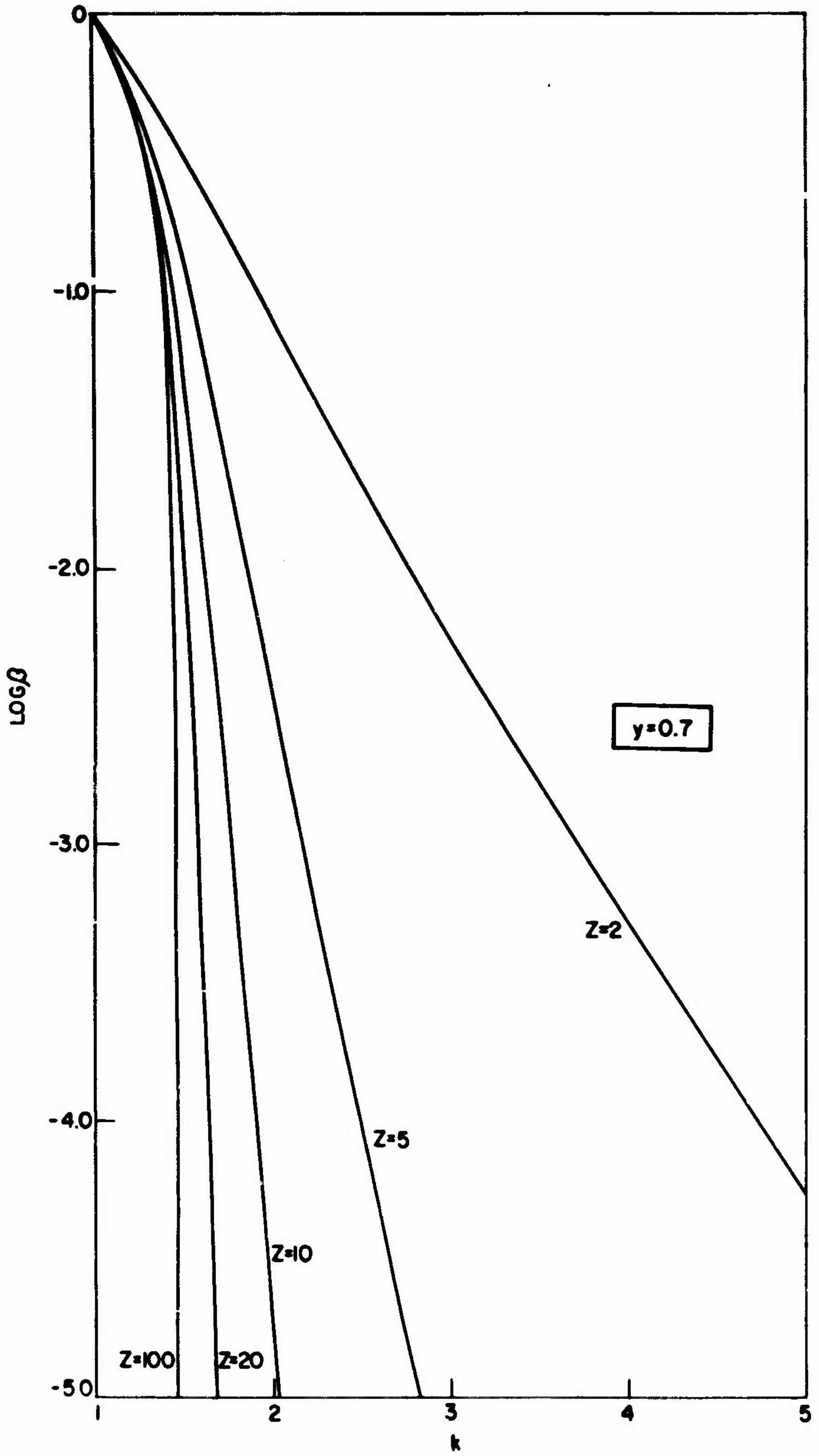

Figure 62. Plot of log β vs k when Eq. (42) is Used and k > 1

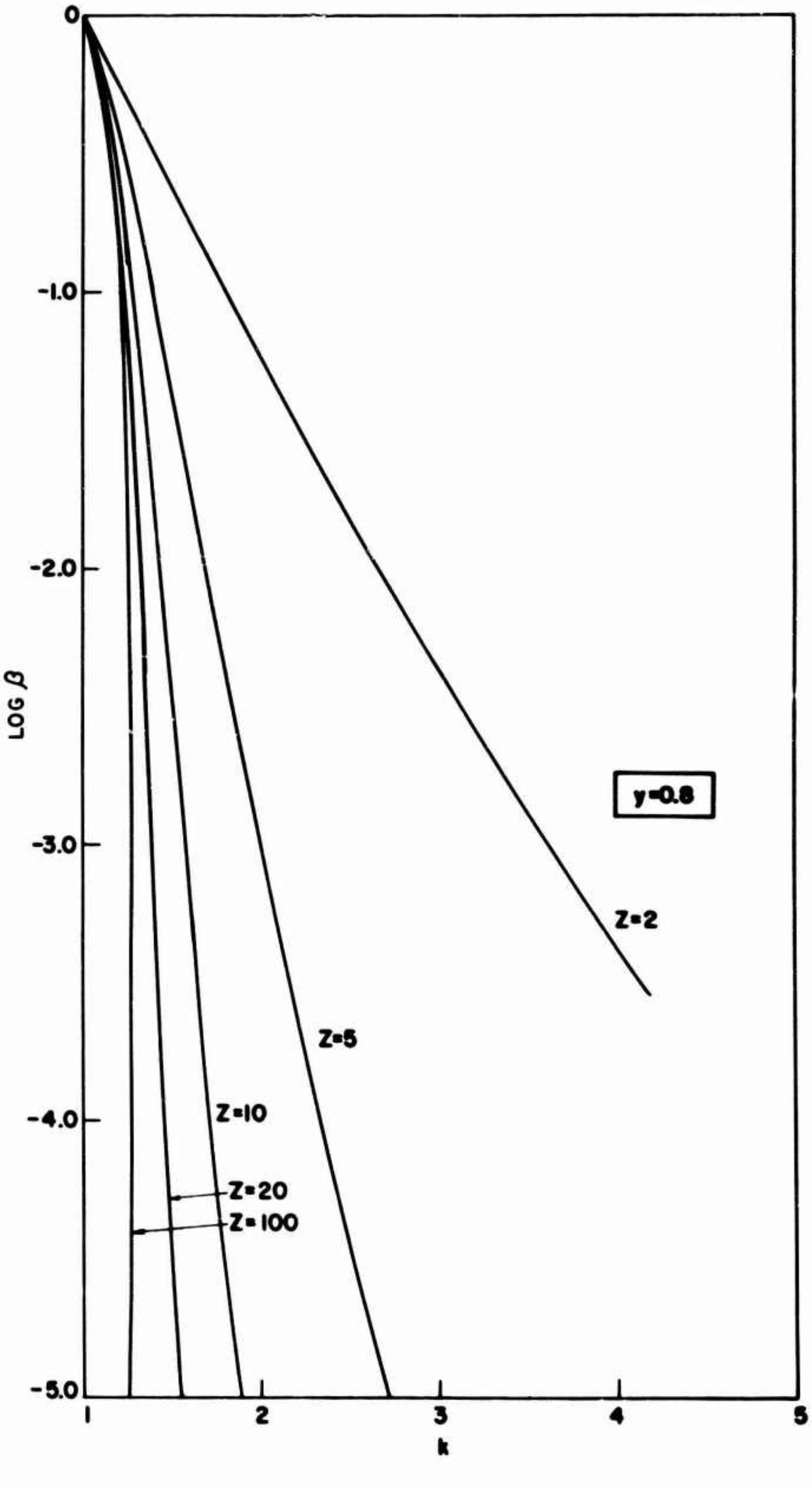

Figure 63. Plot of log β vs k when Eq. (42) is Used and k > 1

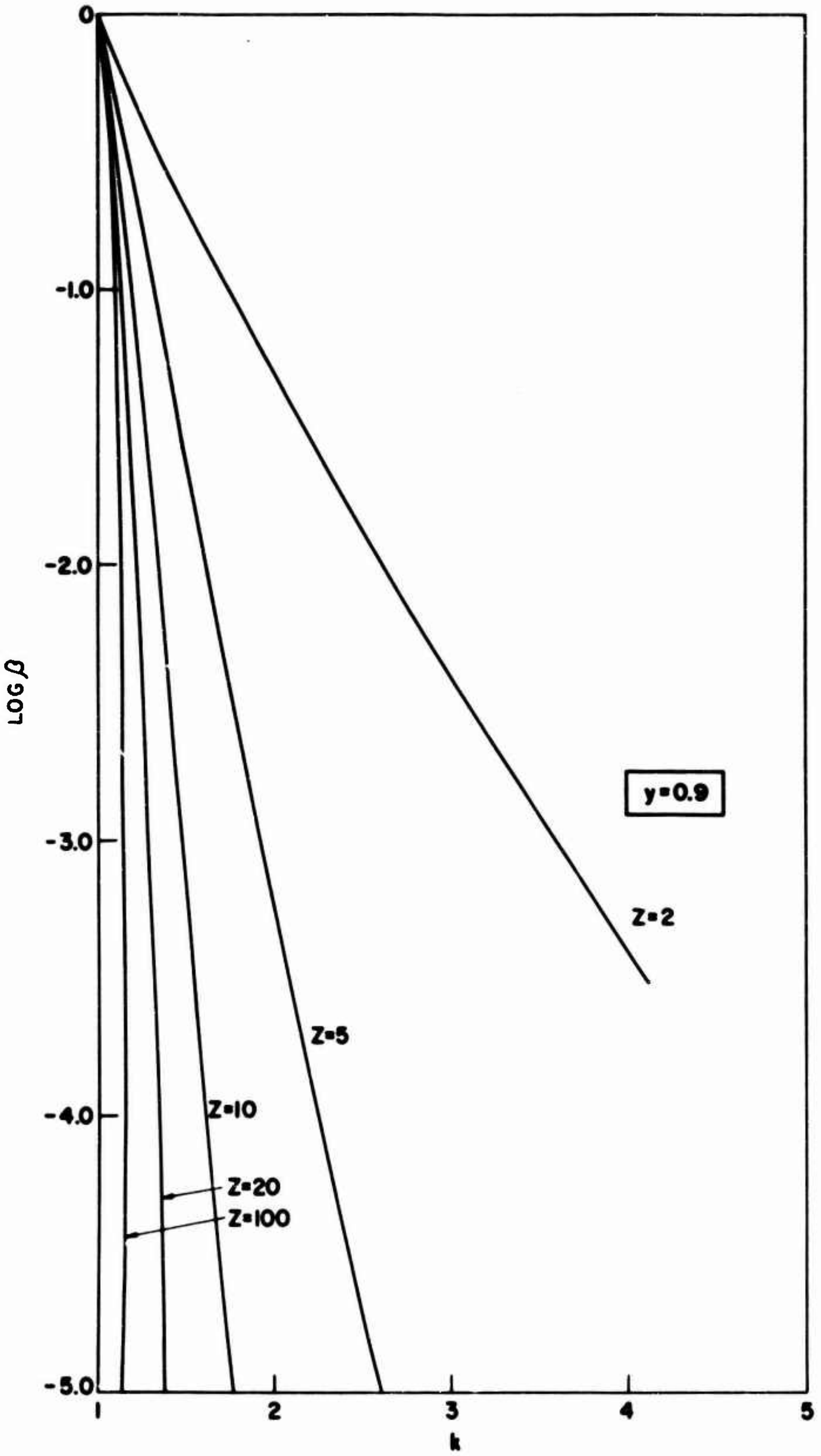

Figure 64. Plot of log β vs k when Eq. (42) is Used and k > 1

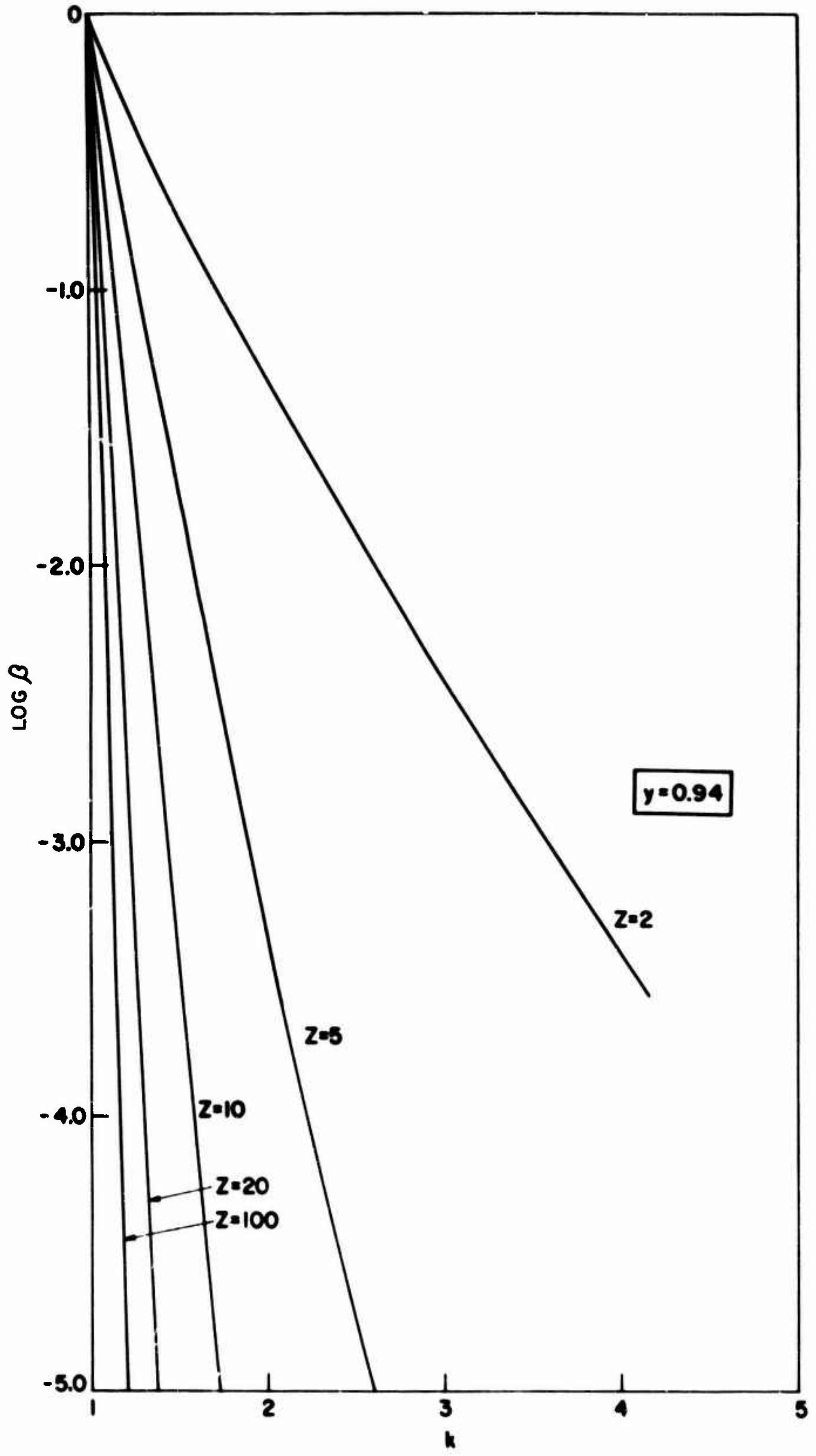

Figure 65. Plot of log β vs k when Eq. (42) is Used and k > 1

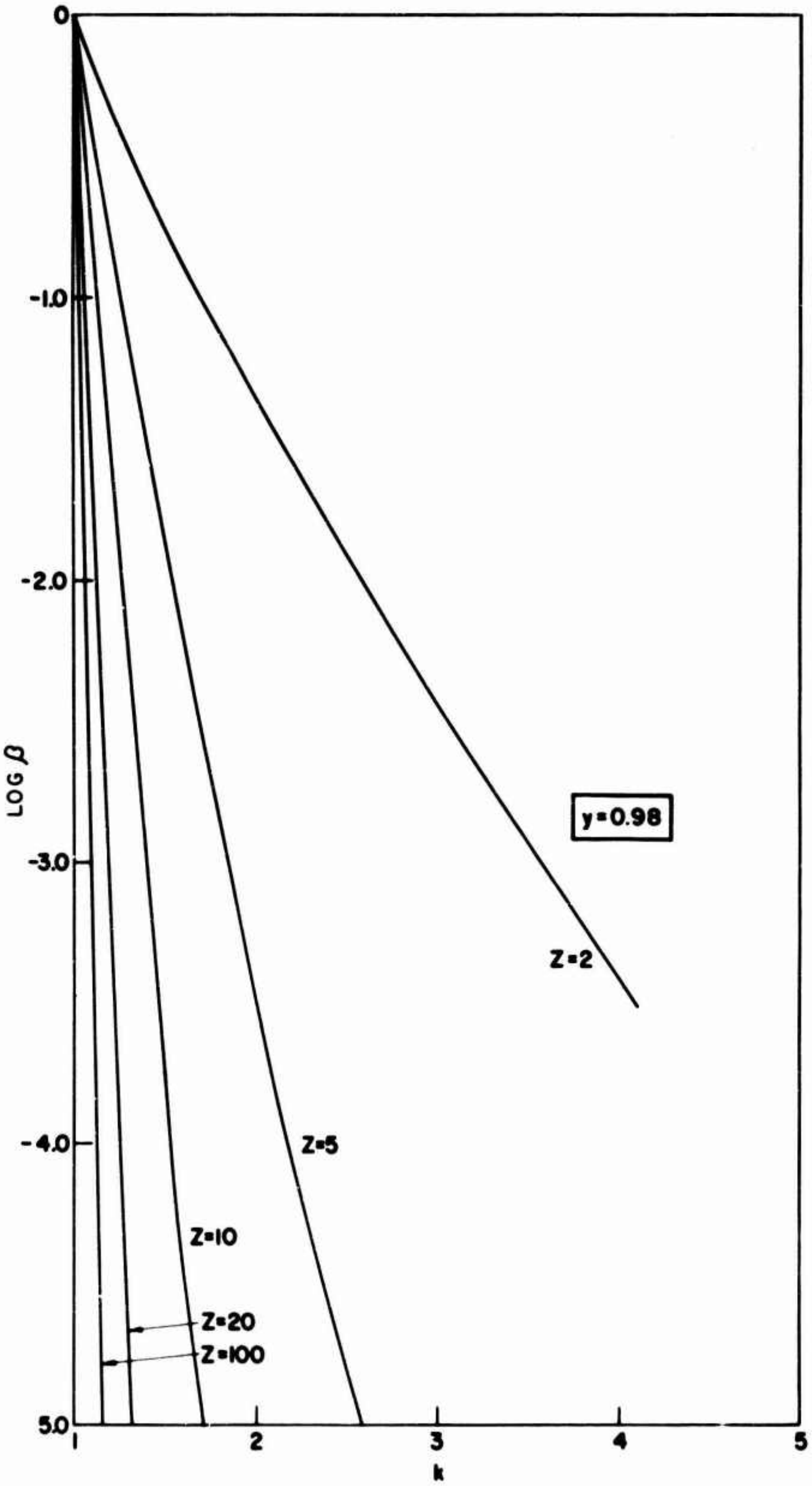

Figure 66. Plot of log β vs k when Eq. (42) is Used and $k > 1$

3. RESULTS

As a result of the effort described in this report several accomplishments have been made in the field of continuous zone refining. An error was found in the overall solute balance equation used in the derivation of the basic equations describing the stripping section of the continuous zone-void system reported by Pfann.[7] The correct solute balance equation was reported (Eq. (20)) and a new set of steady-state equations derived (Appendix D). A difference between the zone-void and the zone-transport system not previously noted was found. This difference, which is in the mathematical definition of the solute concentrations of the product and waste of each system, and the error made by Pfann in the solute balance equation of the stripping section of the zone-void system were used to completely explain the discrepancies between the limits of α and β obtained by using Pfann's[14] steady-state equations for the zone-transport system and Abe's[12] steady-state equations for the zone-transport system. An error in Abe's zone-transport equations due to improperly accounting for the density change due to melting was noted and corrected.

A new continuous zone refining system, the matter transport system, was described.[20] The matter transport system increases the flexibility of design of a zone refining system which can result in increased product purity. Steady-state equations describing the three continuous systems treated herein were rederived with particular attention being paid to terminology and the treatment of the change in density due to melting. The feasibility of describing the matter transport system by the mathematical model of either the zone-void or the zone-transport system was noted, however, the authors have indicated their preference for the zone-transport model wherein the mode of freezing in the terminal zone of the stripping section is taken into account.

The actual values of α and β obtained using the matter transport system will be somewhere between those predicted by the zone-void and the zone-transport systems.

The choice of the optimum physical parameters of a continuous zone-refining system required to produce any given α or β has been greatly simplified by the introduction of nondimensional parameters. The nondimensionalization permits complete description of a zone refining system with a minimum number of parameters. A high speed digital computer can and has been used to obtain results which in graphical form clearly and simply indicate the magnitude of the effect produced by variation of any of these parameters. The nondimensionalization transforms the steady-state equations of each section of a continuous system into a pair of equations which we have called universal equations. The universal equations for the zone-void system and the zone-transport system were derived (Appendices I-L). The universal charts which result from computer computations made by substituting realistic parameter values into the equations are shown in Figures 9-66. With the aid of these charts it can be seen that the difference between the enriching section of the zone-void and zone-transport systems is negligible for $y < 0.9$ and $z > 10$. In the stripping section the difference between the normal and uniform freeze is also negligible for $y < 0.9$ and $z > 10$, however, of more importance is the fact that the curves clearly demonstrate the futility of increasing z over 10.

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Appendix A

DERIVATION OF THE SOLUTE DISTRIBUTION IN A SEMI-INFINITE INGOT AFTER THE PASSAGE OF ONE MOLTEN ZONE, EQ. (3) (AFTER PFANN[2])

The purpose of this derivation is to find an expression which will define the solute concentration in the solid, C, at any plane along a charge after one molten zone has passed. The authors have modified Pfann's original derivation to account for the change in density due to melting. The matter transport phenomenon and its complicating effects on the shape of the charge can be accounted for by the change due to melting.

In order to derive an equation for the solute distribution under these conditions the spacial orientation of the charge and the ratio of the density of the solid to the density of the liquid, ρ_s/ρ_ℓ, must be considered. If Figure 1 is placed in a vertical position, the mathematical treatment is fairly straightforward. If $k < 1$ and $\rho_s > \rho_\ell$ a molten zone can be made to travel downward without fear of breakage due to matter transport, since expansion is taken care of in the first zone. When the molten zone reaches the bottom of the charge the zone contracts on freezing. The equation for the solute concentration C at the plane which exists at any weight of solid material x measured from the beginning of the frozen charge to the freezing interface of the molten zone being passed through the charge is derived as follows:

Let:

C_o = the average solute concentration at any plane in the charge, prior to passage of the molten zone, expressed in weight fraction.

C_ℓ = the solute concentration in the molten zone in weight-fraction.
s = the weight of solute in a zone at any x
s_o = the weight of solute in the zone at $x = 0$
k = effective distribution coefficient
ℓ = weight of liquid in the molten zone

Assume:

1. ℓ is constant
2. the charge is of unit cross-section

When the molten zone moves a distance equivalent to the weight increment dx, a weight of solid, dx, will be frozen out of the zone at the freezing interface and an equal weight of solid will be melted in. The weight of solute frozen out is

$$k C_\ell \, dx \qquad (A\text{-}1)$$

but

$$C_\ell = \frac{s}{\ell} \qquad (A\text{-}2)$$

The weight of solute melting into the zone is

$$C_o \, dx \qquad (A\text{-}3)$$

Therefore the resulting change in s is

$$ds = \left(C_o - \frac{ks}{\ell}\right) dx \qquad (A\text{-}4)$$

or

$$ds + \frac{ks}{\ell} dx = C_o \, dx \qquad (A\text{-}5)$$

Integrating Eq. (A-5) yields

$$e^{\frac{kx}{\ell}} s = \frac{\ell}{k} C_o e^{\frac{kx}{\ell}} \qquad (A\text{-}6)$$

Evaluating Eq. (A-6) between the limits 0 and x

$$s e^{\frac{kx}{\ell}} - s_o = \frac{C_o \ell}{k}\left[e^{\frac{kx}{\ell}} - 1\right] \tag{A-7}$$

since $s_o = C_o\ell$ then

$$s = \left[C_o\ell + \frac{C_o\ell}{k}\left(e^{\frac{kx}{\ell}} - 1\right)\right] e^{-\frac{kx}{\ell}} \tag{A-8}$$

$$s = C_o\ell \, \frac{k - 1}{k} \, e^{-\frac{kx}{\ell}} + \frac{C_o\ell}{k} \tag{A-9}$$

Since $C = \frac{ks}{\ell}$:

$$C = C_o(k-1) \, e^{-\frac{kx}{\ell}} + C_o \tag{A-10}$$

or

$$\frac{C}{C_o} = 1 - (1-k) \, e^{-\frac{kx}{\ell}} \tag{3}$$

Appendix B

DERIVATION OF THE ULTIMATE DISTRIBUTION IN A BATCH SYSTEM, EQS. (4) – (6) (AFTER PFANN[2])

Consider Figure 1; assume that a sufficient number of passes have been passed through the charge to establish the ultimate distribution. Under these conditions when a molten zone is passed through the ingot it does not change the solute distribution. Using the assumptions and definitions of terms as given in Appendix A, the solute concentration in the molten zone, $C_\ell(x)$, is defined as $C(x)/k$. $C_\ell(x)$ is also given by Eq. (B-1). Thus

$$C_\ell(x) = \frac{1}{\ell} \int_x^{x+\ell} C(x)\,dx \tag{B-1}$$

or

$$C(x) = \frac{k}{\ell} \int_x^{x+\ell} C(x)\,dx \tag{B-2}$$

The solution of Eq. (B-2) is

$$C(x) = Ae^{Bx} \tag{4}$$

substituting Eq. (4) in Eq. (B-2) and integrating yields

$$Ae^{Bx} = \frac{Ak}{B\ell} e^{Bx}(e^{B\ell} - 1) \qquad \text{(B-3)}$$

Solving Eq. (B-4) for $x = 0$ gives

$$k = \frac{B\ell}{e^{B\ell} - 1} \qquad (5)$$

If the whole ingot is considered then Eq. (B-2) can be written as

$$C(x) = \frac{1}{L} \int_0^L C(x)\, dx \qquad \text{(B-4)}$$

From Eqs. (4) and (B-4), Eq. (6) is readily obtained thus

$$A = \frac{C_0 BL}{e^{BL} - 1} \qquad (6)$$

Appendix C

DERIVATION OF THE STEADY-STATE EQUATIONS FOR THE ENRICHING SECTION OF THE ZONE-VOID SYSTEM, EQS. (12) - (15) (AFTER PFANN[7])

When the enriching section of the zone-void system has reached the steady state, removal of product at the start of each pass form a void. Passing the void through the section shifts the solute distribution C(x) as shown in Figure 4. When a molten zone is passed through the section it shifts the solute distribution back to the steady state.

Under these conditions the derivation proceeds as follows:

Let:

ℓ = the weight of liquid material in the molten zone that is maintained molten and caused to move by a moving heater.

$h - \ell$ = weight of product collected per pass.

h = the weight of material equal to the weight of liquid material that is maintained molten and caused to move by a moving heater plus the weight of product collected per pass.

L_e = weight of material in the column up to the plane where the solute concentration is kC_f.

The amount of solute in a molten zone having its freezing interface at the plane x is $C(x)\ell/k$. This amount of solute is equal to the same amount of solute that was melted into the molten zone minus the amount that had frozen out. Thus

$$C(x)\,\frac{\ell}{k} = \int_{h-\ell}^{x+h} C(x)\,dx - \int_{0}^{x} C(x)\,dx \qquad \text{(C-1)}$$

The solution of Eq. (C-1) is

$$C(x) = A_1 + A_2 e^{B_e x} \tag{C-2}$$

Substituting Eq. (C-2) into Eq. (C-1) and integrating yields

$$\frac{\ell}{k}\left(A_1 + A_2 e^{B_e x}\right) = A_1 \ell + \frac{A_2}{B_e}\left[1 - e^{B_e(h-\ell)}\right] + \frac{A_2 e^{B_e x}}{B_e}\left(e^{B_e h} - 1\right) \tag{C-3}$$

There are two sets of terms on both sides of Eq. (C-3). One set of terms contains the variable in the form $e^{B_e x}$; the other set contains constant terms only. In order for the equation to hold, the $e^{B_e x}$ terms have to be equal and the constant terms must be equal.

Equating the $e^{B_e x}$ terms and simplifying yields

$$e^{B_e h} = 1 + \frac{B_e \ell}{k} \tag{13}$$

when the constant terms are equated and rearranged

$$0 = A_2 \omega - A_1 \tag{C-4}$$

where

$$\omega = \frac{k}{B_e \ell (1-k)}\left[1 - e^{B_e(h-\ell)}\right] \tag{14}$$

Using Eq. (C-4) and the assumed boundary condition $C(L_e) = A_1 + A_2 e^{B_e L_e}$ expressions for A_1 and A_2 can be determined. Thus

$$A_1 = \frac{kC_f \omega}{e^{B_e L_e} + \omega} \tag{C-5}$$

$$A_2 = \frac{kC_f}{e^{B_e L_e} + \omega} \tag{C-6}$$

The expression for the solute concentration in the product is given by:

$$C_p(h-\ell) = \int_0^{h-\ell} \left(A_1 + A_2 e^{B_e x}\right) dx \qquad \text{(C-7)}$$

Integration of Eq. (C-7) shows

$$C_p = A_1 + \frac{A_2}{B_e(h-\ell)} \left[e^{B_e(h-\ell)} - 1 \right] \qquad \text{(C-8)}$$

From Eqs. (C-5), (C-6), and (C-8) it can be shown that

$$e^{B_e L_e} = \omega\left(\frac{\psi}{\alpha} - 1\right) \qquad \text{(C-9)}$$

or

$$L_e = \frac{1}{0.434\ B_e} \log \omega\left(\frac{\psi}{\alpha} - 1\right) \qquad \text{(12)}$$

where

$$\psi = \frac{kh - \ell}{h - \ell} \qquad \text{(15)}$$

Appendix D

DERIVATION OF THE CORRECTED STEADY-STATE EQUATIONS FOR THE STRIPPING SECTION OF THE ZONE-VOID, SYSTEM, EQS. (21) - (24)

The steady-state solute distribution C(x) for the stripping section of the zone-void system is shown in Figure 5. The shift of the solute distribution due to passing a void through the system is indicated by the dashed curve. The travel of the molten zone through the system shifts the solute distribution back to the steady state. C(x) is made up of two parts joined at $x = L_s$, the zone refining portion and the normal freezing portion.

The derivation of the steady-state equations which define such a system is as follows: Let

w = weight of waste collected per pass

ℓ = weight of liquid material in the molten zone that is maintained molten and caused to travel by a moving heater

h = a weight of material equal to $\ell \dfrac{\rho_s}{\rho_\ell}$

In the zone refining portion of C(x) the amount of solute in the molten zone, whose freezing interface is at x, is given by:

$$\frac{\ell C(x)}{k} = \ell C_f + \int_h^{x+h} C[x-(h-\ell+w)]\,dx - \int_0^x C(x)\,dx \qquad \text{(D-1)}$$

which after manipulation yields

$$\frac{\ell C(x)}{k} = \ell C_f + \int_{\ell - w}^{x+\ell-w} C(x)\,dx - \int_0^x C(x)\,dx \qquad \text{(D-2)}$$

The solution of Eq. (D-2) is

$$C = A_1 + A_2 e^{B_s x} \qquad \text{(D-3)}$$

Substituting Eq. (D-3) into Eq. (D-2) and integrating yields

$$A_1 \cdot A_2 e^{B_s x} - \frac{k}{\ell} \left\{ \ell C_f + \frac{A_2}{B}\left[1 - e^{B_s(\ell-w)}\right] + \frac{A_2}{B} e^{B_s x}\left[e^{B_s(\ell-w)} - 1\right] \right\} \qquad \text{(D-4)}$$

Equating the $e^{B_s x}$ terms of Eq. (D-4) and simplifying gives

$$e^{B_s(\ell-w)} = 1 + \frac{B_s \ell}{k} \qquad (22)$$

Equating the constant terms of Eq. (D-4) and using Eq. (22) yields

$$kC_f = A_1 + A_2 \qquad \text{(D-5)}$$

Equation (D-5) is a boundary condition describing the solute concentration at $x = 0$. In order to solve for A_1 and A_2, a second expression for A_1 and A_2 is needed. The solute balance over the entire cycle is such an expression. Thus:

$$\ell C_f = \int_0^{\ell - w} C(x)\,dx + w\beta C_f \qquad \text{(D-6)}$$

Using Eq. (D-3), Eq. (D-6) can be rewritten

$$C_f\left[\frac{\ell - \beta w}{\ell - w}\right] = A_1 + \frac{A_2}{B_s(\ell - w)}\left[e^{B_s(\ell-w)} - 1\right] \qquad \text{(D-7)}$$

From Eqs. (D-7) and (D-5) are obtained

$$A_1 = kC_f \mu\beta \qquad \text{(D-8)}$$

and

$$A_2 = kC_f(1 - \beta\mu) \quad \text{(D-9)}$$

where

$$\mu = \frac{w}{\ell - k(\ell - w)} \quad \text{(24)}$$

It has been assumed that Eq. (D-3) describes the solute concentration in the charge up to the plane at weight of material L_s. The solute concentration in the molten zone from which the solid at L_s is freezing has the solute concentration $C(L_s)/k$. Assuming that between $x = L_s$ and $x = L_s + \ell$ a normal freeze takes place, then the normal freezing equation (Eq. (2)) describes the solute concentration over this distance, Figure 5. Since a weight of material equal to w is removed from the waste end of the section in order to form a void during each pass, then the solute concentration in the plane $L_s + \ell - w$ is equal to $C_w = \beta C_f$. The solute concentration in the solid at the plane $L_s + \ell - w$ is kC_f. Therefore since:

$$C(L_s) = A_1 + A_2 e^{B_s L_s} \quad \text{(D-10)}$$

and the normal freezing equation is

$$C = kC_o(1-g)^{k-1} \quad \text{(2)}$$

combining Eqs. (D-10) and (2) gives

$$C_w = \beta C_f = \frac{C(L_s)}{k}\left(1 - \frac{\ell - w}{\ell}\right)^{1-k} \quad \text{(D-11)}$$

or

$$C(L_s) = \beta\delta C_f \quad \text{(D-12)}$$

where

$$\delta = k\left(\frac{w}{\ell}\right)^{1-k} \quad \text{(23)}$$

Substituting Eqs. (D-8), (D-9), and (D-12) in Eq. (D-10) gives

$$e^{B_s L_s} = \frac{\beta(\delta - k\mu)}{k(1-\beta\mu)} \tag{D-13}$$

or

$$L_s = \frac{1}{0.434\, B_s} \log \left[\frac{\beta(\delta - k\mu)}{k(1-\beta\mu)} \right] \tag{21}$$

Appendix E

DERIVATION OF THE STEADY-STATE EQUATIONS FOR THE ENRICHING SECTION OF THE ZONE-TRANSPORT SYSTEM USING ABE'S[12] TECHNIQUE

Abe points out that when the steady state has been obtained, if we consider the two zones a and b (Figure E1), the total amount of solute in these two zones when a is liquid and b is solid is equal to the total amount of solute in the zones when a is solid and b is liquid. This equality assumes that the shape of the ingot is a rectangular parallelopiped and that surface tension is negligible. This expression is written

$$\frac{C(x)\ell}{k} + \int_{x}^{x+P+\ell} C(x+P+\ell)\,dx = \int_{x}^{x+P+\ell} C(x)\,dx + \frac{C(x+P+\ell)\,\ell}{k} \qquad \text{(E-1)}$$

or

$$C(x+P+\ell) - C(x) = \frac{k}{\ell} \int_{x}^{x+P+\ell} [\,C(x+P+\ell) - C(x)\,dx] \qquad \text{(E-2)}$$

The rate of change of solute in the molten zone is:

$$d\left[\frac{C(x)\ell}{k}\right] = [\,C(x+P+\ell) = C(x)]\,dx \qquad \text{(E-3)}$$

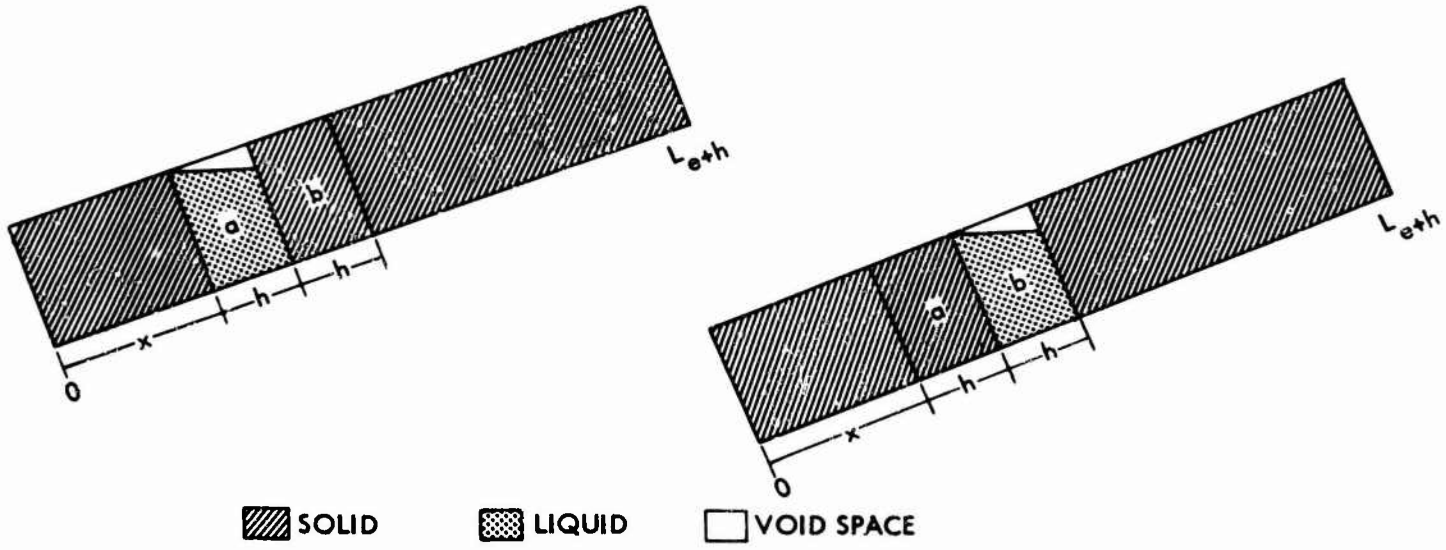

Figure E1. Zone-Transport System Enriching Section (After T. Abe[12])

The solution of Eq. (E-2) is

$$C(x+P+\ell) - C(x) = Ae^{B_e x} \qquad \text{(E-4)}$$

Substituting Eq. (E-4) into Eq. (E-2) and simplifying yields

$$e^{B_e(P+\ell)} = \frac{B_e \ell}{k} + 1 \qquad \text{(33)}$$

Equation (E-3) can be rewritten thus

$$\frac{dC(x)}{dx} = \frac{k}{\ell}\left[C(x+P+\ell) - C(x)\right] \qquad \text{(E-5)}$$

Substituting Eq. (E-4) into Eq. (E-5) and integrating between the limits 0 and x yields

$$C(x) = C(o) + \frac{Ak}{B\ell}\left(e^{B_e x} - 1\right) \qquad \text{(E-6)}$$

Assuming the boundary condition $C(L_e) = kC_f$ and using Eq. (E-6) it can be shown that

$$L_e = \frac{1}{B_e} \ln \left\{1 + \frac{B_e \ell}{Ak}\left[kC_f - C(o)\right]\right\} \qquad \text{(E-7)}$$

By definition

$$\alpha C_f = C_p = \frac{1}{P+\ell}\int_0^{P+\ell} C(x)\,dx \qquad \text{(E-8)}$$

From Eqs. (E-8) and (E-6) it can be shown that

$$C_p = C(o) - \frac{Ak}{B_e \ell} + \frac{A}{B_e(P+\ell)} \qquad \text{(E-9)}$$

Consideration of the gain and loss of material in the two regions $0 < x < P+\ell$, and $P+\ell < x < 2(P+\ell)$ when they are molten and solid respectively yields

$$C_p \ell + \int_{P+\ell}^{2(P+\ell)} C(x)\,dx = \int_0^{P+\ell} C(x)\,dx + \frac{C(P+\ell)\ell}{k} \tag{E-10}$$

Using Eq. (E-8) and performing the necessary integration and simplification it can be shown that Eq. (E-10) can be rewritten as

$$C_p + \frac{A}{k} = \frac{C(P+\ell)}{k} \tag{E-11}$$

When $x = 0$, Eq. (E-4) becomes

$$C(P+\ell) - C(o) = A \tag{E-12}$$

Substituting Eq. (E-12) into Eq. (E-11), using Eq. (E-9) to substitute for $C(o)$ and solving for A yields

$$A = \frac{\alpha C_f B_e \ell (1-k)(P+\ell)}{\ell - k(P+\ell)} \tag{E-13}$$

Using Eq. (E-9), Eq. (E-7) can be rewritten

$$L_e = \frac{1}{B_e} \ln \left[\frac{B_e \ell}{Ak} (kC_f - C_p) + \frac{\ell}{k(P+\ell)} \right] \tag{E-14}$$

From Eq. (E-13)

$$\frac{B_e \ell}{Ak} = \frac{\ell - k(P+\ell)}{k\alpha C_f (1-k)(P+\ell)} \tag{E-15}$$

From Eqs. (E-15) and (E-14) it can be shown that

$$L_e = \frac{1}{B_e} \ln \left[\frac{\ell}{k(P+\ell)} \left(\frac{[\ell - k(P+\ell)](k-\alpha)}{\ell\alpha(1-k)} + 1 \right) \right] \tag{E-16}$$

or

$$e^{B_e L_e} = \frac{\ell}{k(P+\ell)} \left(\frac{[\ell - k(P+\ell)](k-\alpha)}{\ell\alpha(1-k)} + 1 \right) \tag{E-17}$$

Appendix F

DERIVATION OF THE STEADY-STATE EQUATIONS FOR THE STRIPPING SECTION OF THE ZONE-TRANSPORT SYSTEM USING ABE'S[12] TECHNIQUE

As in Appendix E, consider the amount of solute in the two zones c and d, of Figure F1, when c is liquid and d is solid and when c is solid and d is liquid. Assume the ingot shape is a parallelopiped except in the molten zone where the shape of the liquid zone is as shown. Then the solute balance can be expressed as

$$\frac{C(x)(h+w)}{k} + \int_{x}^{x+h} C(x+h)\,dx = \int_{x}^{x+h} C(x)\,dx + \frac{(h+w)\,C(x+h)}{k} \qquad (F\text{-}1)$$

or

$$C(x+h) - C(x) = \frac{k}{h+w} \int_{x}^{x+h} \Big(C(x+h) - C(x)\Big)\,dx \qquad (F\text{-}2)$$

For the molten zone the rate of change of solute is

$$d\left(\frac{C(x)[h+w]}{k}\right) = \Big(C(x+h) - C(x)\Big)\,dx \qquad (F\text{-}3)$$

The solution of Eq. (F-2) is

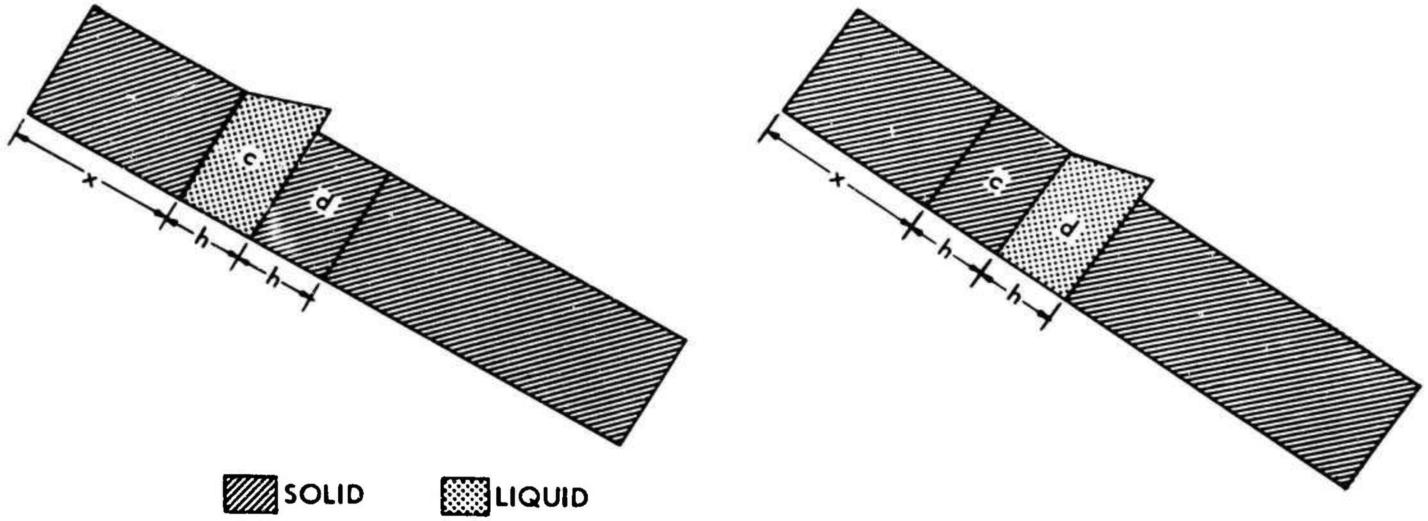

Figure F1. Zone-Transport System Stripping Section (After T. Abe[12])

$$C(x+h) - C(x) = Ae^{B_s x} \qquad \text{(F-4)}$$

From Eqs. (F-4) and (F-2) it can be shown that

$$e^{B_s h} = \frac{B_s(h+w)}{k} + 1 \qquad \text{(F-5)}$$

Equation (F-3) can be rewritten thus

$$\frac{dC(x)}{dx} = \frac{k}{h+w}\Big(C(x+h) - C(x)\Big) \qquad \text{(F-6)}$$

Substituting Eq. (F-4) in (F-6) and integrating between 0 and x yields

$$C(x) = C(o) + \frac{Ak}{B_s(h+w)}\left[e^{B_s x} - 1\right] \qquad \text{(F-7)}$$

At $x = 0$ the following boundary condition holds

$$C(o) = kC_f \qquad \text{(F-8)}$$

By definition

$$Cw = \frac{C(L_s)}{k} \qquad \text{(F-9)}$$

and

$$L'_s = L_s + h \qquad \text{(F-10)}$$

From Eqs. (F-7), (F-8) and (F-9) it can be shown that

$$Cw = \frac{C_{L_s}}{k} = \beta C_f = C_f + \frac{A}{B_s(h+w)}\left[e^{B_s L_s} - 1\right] \qquad \text{(F-11)}$$

Solving Eq. (F-11) for L_s

$$L_s = \frac{1}{B_s} \ell n \left(1 + \frac{B_s C_f (B-1)(h+w)}{A}\right) \qquad \text{(F-12)}$$

For the two zones $L_s = \ell < x < L_s$ and $L_s < x < L'_s$ the gain and loss of material when they are molten and solid respectively can be expressed as

$$w\beta C_f + \int_{L_s - h}^{L_s} C(x)\, dx = \frac{(h+w) C_{(L_s - h)}}{k} \qquad \text{(F-13)}$$

Using Eqs. (F-5) and (F-7) and performing the indicated integration Eq. (F-13) becomes

$$\frac{A}{B}\left(1 - \frac{kh}{h+w}\right) = C_f \left(w(1-\beta) + h(1-k)\right) \qquad \text{(F-14)}$$

solving for A yields

$$A = \frac{B_s C_f (h+w)(w[1-\beta] + h[1-k])}{w + h(1-k)} \qquad \text{(F-15)}$$

Substituting Eq. (F-15) in Eq. (F-12) and simplifying yields

$$L_s = \frac{1}{B_s} \ell n \left[\frac{\beta h(1-k)}{h(1-k) + w(1-\beta)}\right] \qquad \text{(F-16)}$$

or

$$e^{B_s L_s} = \frac{\beta h(1-k)}{h(1-k) + w(1-\beta)} \qquad \text{(F-17)}$$

Appendix G

DERIVATION OF THE STEADY-STATE EQUATIONS FOR THE ENRICHING SECTION OF THE ZONE-TRANSPORT SYSTEM USING PFANN'S[14] TECHNIQUE

This derivation uses the same mathematical technique shown in Appendix C. The modifications are imposed by the variation in boundary conditions and terminology. Thus the amount of solute in the molten zone whose freezing interface is at the plane x is $C(x)\ell/k$ and is given by the solute balance expression, thus

$$\frac{C(x)\ell}{k} = \int_{o}^{x+P+\ell} C(x)\,dx - \int_{o}^{x} C(x)\,dx - \frac{P}{P+\ell}\int_{o}^{P+\ell} C(x)\,dx \qquad \text{(G-1)}$$

The solution of Eq. (G-1) is

$$C = A_1 + A_2 e^{B_e x} \qquad \text{(G-2)}$$

Substituting Eq. (G-2) in Eq. (G-1) and integrating yields

$$\begin{aligned} A_1 \frac{\ell}{k} + \frac{\ell}{k}\left(A_2 e^{B_e x}\right) = {} & e^{B_e x}\left[\frac{A_2}{B_e} e^{B_e(P+\ell)}\right] - \frac{A_2}{B_e} e^{B_e x} + \frac{A_2}{B_e} \\ & - \frac{A_2}{B_e} e^{B_e(P+\ell)} + A_1\ell - \frac{A_2\ell}{B_e(P+\ell)} + \frac{A_2\ell}{B_e(P+\ell)} e^{B_e(P+\ell)} \end{aligned} \qquad \text{(G-3)}$$

Equating the $e^{B_e x}$ terms Eq. (G-3) gives

$$e^{B_e(P+\ell)} = \frac{B_e \ell}{k} + 1 \tag{33}$$

Equating the constant terms in Eq. (G-3) yields

$$0 = A_2 \omega - A_1 \tag{G-4}$$

where

$$\omega = -\frac{P}{(P+\ell)(1-k)} \tag{32}$$

One of the boundary conditions is

$$kC_f = A_1 + A_2 e^{B_e L_e} \tag{G-5}$$

From Eqs. (G-4) and (G-5) it can be shown that

$$A_1 = \frac{kC_f \omega}{e^{B_e L_e} + \omega} \tag{G-6}$$

and

$$A_2 = \frac{kC_f}{e^{B_e L_e} + \omega} \tag{G-7}$$

The solute concentration in the product is

$$C_p = \frac{1}{P+\ell} \int_0^{P+\ell} \left(A_1 + A_2 e^{B_e x} \right) dx \tag{G-8}$$

Integrating Eq. (G-8) and utilizing Eqs. (G-6), (G-7) and (33) to solve for L_e yields

$$e^{B_e L_e} = \frac{\omega k(P+\ell) + \ell}{\alpha(P+\ell)} - \omega \tag{G-9}$$

or

$$L_e = \frac{1}{0.434\ B_e} \log \left[\frac{\omega k(P+\ell) + \ell}{a(P+\ell)} - \omega \right] \tag{31}$$

Appendix H

DERIVATION OF THE STEADY-STATE EQUATIONS FOR THE STRIPPING SECTION OF THE ZONE-TRANSPORT SYSTEM USING PFANN'S[14] TECHNIQUE

In the zone-transport system the waste is withdrawn before the terminal zone begins to freeze. Since back reflection is not considered then, when the density change due to melting is taken into account, the derivation, which is very similar to that given in Appendix D, is as follows:

The amount of solute in a molten zone having its freezing interface at x (Figure H1) is

$$\frac{\ell C(x)}{k} = \ell C_f + \int_{h}^{x+h} C(x - [h - \ell + w])\, dx - \int_{o}^{x} C(x)\, dx \qquad \text{(H-1)}$$

Equation (H-1) can be rewritten as

$$C(x) + \frac{k}{\ell}\left[\ell C_f + \int_{\ell-w}^{x+\ell w} C(x)\, dx - \int_{o}^{x} C(x)\, dx\right] \qquad \text{(H-2)}$$

The solution of Eq. (H-2) is

$$C = A_1 + A_2 e^{B_s x} \qquad \text{(H-3)}$$

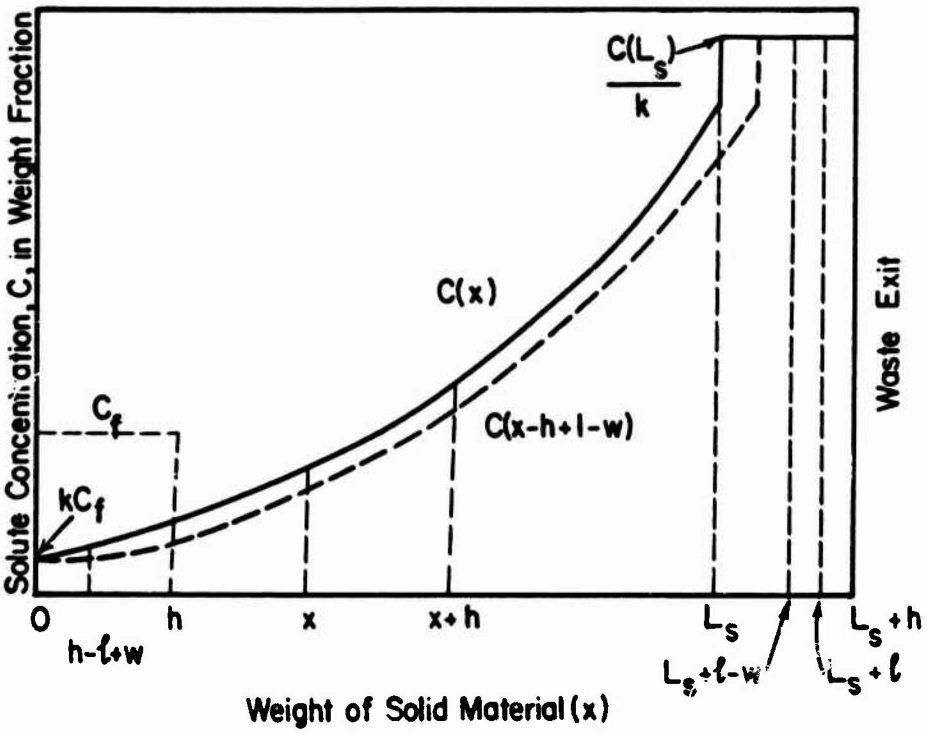

Figure H1. Steady-State Solute Distribution in the Stripping Section of the Zone Transport System when the Terminal Zone Undergoes a Uniform Freeze

Substituting Eq. (H-3) in Eq. (H-2) and integrating gives

$$A_1 + A_2 e^{B_s x} = \frac{k}{\ell}\left[\ell C_f + \frac{A_2}{B_s}\left(1 - e^{B_s(\ell - w)} + \frac{A_2}{B_s} e^{B_s x}\left(e^{B_s(\ell - w)} - 1\right)\right)\right] \qquad \text{(H-4)}$$

Equating the $e^{B_s x}$ terms yields

$$e^{B_s(\ell - w)} \quad 1 + \frac{B_s \ell}{k} \qquad \text{(H-5)}$$

Equating the constant terms of Eq. (H-4) and using Eq. (H-5) gives

$$kC_f = A_1 + A_2 \qquad \text{(H-6)}$$

the boundary condition existing at $x = o$. The solute balance for the entire cycle is

$$\ell C_f = \int_o^{\ell - w} C(x)\,dx + w\beta C_f \qquad \text{(H-7)}$$

From Eqs. (H-3) and (H-7) it can be shown that

$$C_f\left[\frac{\ell - \beta w}{\ell - w}\right] = A_1 + \frac{A_2}{B_s(\ell - w)}\left(e^{B_s(\ell - w)} - 1\right) \qquad \text{(H-8)}$$

Using Eqs. (H-6) and (H-8) it is readily shown that

$$A_1 = kC_f \beta\mu \qquad \text{(H-9)}$$

and

$$A_2 = kC_f(1 - \beta\mu) \qquad \text{(H-10)}$$

where

$$\mu = \frac{w}{\ell - k(\ell - w)} \qquad \text{(H-11)}$$

Substituting Eq. (H-3) in Eq. (H-2) and integrating gives

$$A_1 + A_2 e^{B_s x} = \frac{k}{\ell}\left[\ell C_f + \frac{A_2}{B_s}\left(1 - e^{B_s(\ell-w)} + \frac{A_2}{B_s} e^{B_s x}\left(e^{B_s(\ell-w)} - 1\right)\right)\right] \qquad \text{(H-4)}$$

Equating the $e^{B_s x}$ terms yields

$$e^{B_s(\ell-w)} \quad 1 + \frac{B_s \ell}{k} \qquad \text{(H-5)}$$

Equating the constant terms of Eq. (H-4) and using Eq. (H-5) gives

$$kC_f = A_1 + A_2 \qquad \text{(H-6)}$$

the boundary condition existing at $x = o$. The solute balance for the entire cycle is

$$\ell C_f = \int_o^{\ell-w} C(x)\,dx + w\beta C_f \qquad \text{(H-7)}$$

From Eqs. (H-3) and (H-7) it can be shown that

$$C_f\left[\frac{\ell - \beta w}{\ell - w}\right] = A_1 + \frac{A_2}{B_s(\ell-w)}\left(e^{B_s(\ell-w)} - 1\right) \qquad \text{(H-8)}$$

Using Eqs. (H-6) and (H-8) it is readily shown that

$$A_1 = kC_f \beta\mu \qquad \text{(H-9)}$$

and

$$A_2 = kC_f(1-\beta\mu) \qquad \text{(H-10)}$$

where

$$\mu = \frac{w}{\ell - k(\ell-w)} \qquad \text{(H-11)}$$

At L_s

$$C_{(L_s)} = A_1 + A_2 e^{B_s L_s} \tag{H-12}$$

Because of the method of waste removal

$$C_w = \frac{C_{(L_s)}}{k} = \beta C_f \tag{H-13}$$

From Eqs. (H-9), (H-10), (H-12) and (H-13) it is straightforward to show that

$$L_s = \frac{1}{0.434\ B_s} \log \left(\frac{\beta(1-\mu)}{1-\beta\mu} \right) \tag{H-14}$$

or

$$e^{B_s L_s} = \frac{\beta(1-\mu)}{1-\beta\mu} \tag{H-15}$$

Appendix I

DERIVATION OF THE UNIVERSAL EQUATIONS FOR THE ENRICHING SECTION OF THE ZONE-VOID SYSTEM (EQS. (37) and (38))

The pertinent equations are

$$e^{B_e L_e} = \omega\left(\frac{\psi}{a} - 1\right) \qquad \text{(C-9)}$$

$$e^{B_e h} = 1 + \frac{B_e \ell}{k} \qquad (13)$$

$$\omega = \frac{k}{B_e \ell (1-k)}\left[1 - e^{B_e(h-\ell)}\right] \qquad (14)$$

$$\psi = \frac{kh - \ell}{h - \ell} \qquad (15)$$

where

$$a = \frac{C_\rho}{C_f}$$

rewriting Eqs. (C-9), (13), (14) and (15)

$$e^{Bh\frac{L_e}{h}} = \omega\left(\frac{\psi}{\alpha} - 1\right) \tag{I-1}$$

$$e^{Bh} = 1 + Bh \cdot \frac{\ell}{h} \cdot \frac{1}{k} \tag{I-2}$$

$$\omega = \frac{k}{1 - k} \cdot \frac{1}{Bh \cdot \frac{\ell}{h}} \left[1 - e^{Bh\left(1 - \frac{\ell}{h}\right)}\right] \tag{I-3}$$

$$\psi = \frac{k - \frac{\ell}{h}}{1 - \frac{\ell}{h}} \tag{I-4}$$

Using the equalities $Bh = v$, $\frac{\ell}{h} = y$, $\frac{L}{h} = z$ to rewrite Eqs. (I-1) - (I-4) yields respectively

$$e^{vz} = \omega\left(\frac{\psi}{\alpha} - 1\right) \tag{I-5}$$

$$e^{v} = 1 + \frac{vy}{k} \tag{I-6}$$

$$\omega = \frac{k}{1 - k} \cdot \frac{1}{vy} \left[1 - e^{v(1-y)}\right] \tag{I-7}$$

$$\psi = \frac{k - y}{1 - y} \tag{I-8}$$

Substituting Eqs. (I-7) and (I-8) in Eq. (I-9) and solving for α gives Eq. (38) thus

$$\alpha = \frac{\frac{k - y}{1 - y}}{1 + \frac{1 - k}{k}\left(\frac{vye^{vz}}{1 - e^{v(1-y)}}\right)} \tag{38}$$

rearranging Eq. (I-6) [illegible] Eq. (37).

$$k = \frac{vy}{e^{v} - 1} \tag{37}$$

Appendix J

DERIVATION OF THE UNIVERSAL EQUATIONS FOR THE STRIPPING SECTION OF THE ZONE–VOID SYSTEM

The basic equations when the terminal zone freezes by a normal freeze are

$$e^{B_s L_s} = \frac{\beta(\delta - k\mu)}{k(1-\beta\mu)} \tag{D-12}$$

$$e^{B_s(\ell - w)} = 1 + \frac{B_s \ell}{k} \tag{22}$$

$$\delta = k\left(\frac{w}{\ell}\right)^{1-k} \tag{23}$$

and

$$\mu = \frac{w}{\ell - k(\ell - w)} \tag{24}$$

where

$$\beta = \frac{C_w}{C_f}$$

Letting $B_s\ell = v$, $y = \frac{\ell - w}{\ell}$, and $z = \frac{L_s}{\ell}$ Eqs. (D-12), (22), (23) and (24) can be rewritten respectively as

$$e^{vz} = \frac{(\delta - k\mu)}{k(1-\alpha\mu)} \tag{J-1}$$

$$e^{vy} = 1 + \frac{v}{k} \tag{J-2}$$

$$\delta = k(1-y)^{1-k} \tag{J-3}$$

$$\mu = \frac{(1-y)}{(1-ky)} \tag{J-4}$$

Substituting Eqs. (J-4) and (J-3) in Eq. (J-1) and solving for β gives

$$\beta = \frac{e^{vz}(1-ky)}{(1-ky)(1-y)^{1-k} + e^{vz}(1-y) - (1-y)} \tag{40}$$

rearranging Eq. (J-2) yields

$$k = \frac{v}{e^{vy} - 1} \tag{39}$$

Appendix K

DERIVATION OF THE UNIVERSAL EQUATIONS FOR THE ENRICHING SECTION OF THE ZONE-TRANSPORT SYSTEM

The pertinent equations are

$$e^{B_e L_e} = \frac{\omega k(P+\ell) + \ell}{\alpha\,(P+\ell)} - \omega \qquad \text{(G-9)}$$

$$e^{B_e(P+\ell)} = 1 + \frac{B_e \ell}{k} \qquad (33)$$

and

$$\omega = -\frac{P}{(P+\ell)(1-k)} \qquad (32)$$

Letting $B_e(P+\ell) = v$, $\frac{\ell}{P+\ell} = y$ and $\frac{L_e}{P+\ell} = z$, Eqs. (G-9), (33) and (32) can be rewritten respectively

$$e^{vz} = \frac{k\omega + y}{\alpha} - \omega \qquad \text{(K-1)}$$

$$e^{v} = \frac{vy}{k} + 1 \qquad \text{(K-2)}$$

and

$$\omega = \frac{y - 1}{1 - k} \tag{K-3}$$

Substituting Eq. (K-3) into Eq. (K-1) and solving for α yields

$$\alpha = \frac{y - k}{e^{vz}(1-k) + y - 1} \tag{41}$$

rewriting Eq. (K-2) gives

$$k = \frac{vy}{e^{v} - 1} \tag{37}$$

Deriving Eqs. (41) and (37) from the basic equations which result when the zone-transport steady-state equations are derived by Abe's technique (Appendix E) can be accomplished as follows.

$$e^{B_e L_e} = \frac{\ell}{k(P+\ell)} \left(\frac{\left[\ell - k(P+\ell)\right](k-\alpha)}{\ell\alpha(1-k)} + 1 \right) \tag{E-17}$$

$$e^{B_e(P+\ell)} = 1 + \frac{B_e \ell}{k} \tag{33}$$

When, as above, $B_e(P+\ell) = v$, $\frac{\ell}{P+\ell} = y$ and $\frac{L_e}{P+\ell} = z$, Eq. (E-17)can be rewritten

$$e^{vz} = \frac{y}{k} \left(\frac{\left(1 - \frac{k}{y}\right)(k-\alpha)}{\alpha(1-k)} + 1 \right) \tag{K-4}$$

Solving Eq. (K-4) for α yields Eq. (41). Thus

$$\alpha = \frac{y - k}{e^{vz}(1-k) + y - 1} \tag{41}$$

It was shown above that Eq. (33) can be transformed into Eq. (37). Therefore, when carried to the universal equation form, the identity of the results of Abe's and Pfann's derivation techniques is obvious.

Appendix L

DERIVATION OF THE UNIVERSAL EQUATIONS FOR THE STRIPPING SECTION OF THE ZONE–TRANSPORT SYSTEM (EQS. (39) AND (42))

The basic equations are

$$e^{B_s L_s} = \frac{\beta(1-\mu)}{1-\beta\mu} \tag{H-15}$$

$$e^{B_s(\ell-w)} = 1 + \frac{B_s\ell}{k} \tag{35}$$

$$\mu = \frac{w}{k(w-\ell)+\ell} \tag{36}$$

Letting $B_s\ell = v$, $\frac{\ell-w}{\ell} = y$ and $\frac{L_s}{\ell} = z$, Eqs. (H-15), (35) and (36) can be rewritten

$$e^{vz} = \frac{\beta(1-\mu)}{1-\beta\mu} \tag{L-1}$$

$$e^{vy} = 1 + \frac{v}{k} \tag{L-2}$$

$$\mu = \frac{1-y}{1-ky} \tag{L-3}$$

Substituting Eq. (L-3) in Eq. (L-1) and solving for β yields

$$\beta = \frac{e^{vz}}{1 + \frac{1-y}{1-ky} e^{vz} - 1} \tag{42}$$

Equation (L-2) can be rewritten as

$$k = \frac{v}{e^{vy} - 1} \tag{39}$$

Equations (39) and (42) can also be derived from Abe's derivation of the steady-state equations for the zone-transport system stripping section (Appendix F)

The basic equations then, are

$$e^{B_s L_s} = \frac{\beta h(1-k)}{h(1-k) + w(1-\beta)} \tag{F-17}$$

$$e^{B_s h} = \frac{B_s(h+w)}{k} + 1 \tag{F-5}$$

Use of the identities for v, y and z (Table 4) permits the rewriting of Eqs. (F-17) and (F-5).

$$e^{vz} = \frac{\beta y(1-k)}{y(1-k) + (1-\beta)(1-y)} \tag{L-4}$$

$$k = \frac{v}{e^{vy} - 1} \tag{39}$$

Solving (L-4) for β yields

$$\beta = \frac{e^{vz}}{1 + \left(\frac{1-y}{1-ky}\right)(e^{vz} - 1)} \tag{42}$$

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