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Diffusion Across the Modified Polyethylene Separator GX in the Heat-Sterilizable AgO-Zn Battery

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Models of diffusion across an inert membrane have been studied using the computer program CINDA. The models were constructed to simulate various conditions obtained in the consideration of the diffusion of $Ag (OH)_2^-$ ions in the AgO-Zn battery. The effects on concentrations across the membrane at the steady state and on the fluxout as a function of time were used to examine the consequences of stepwise reducing the number of sources of ions, of stepwise blocking the source and sink surfaces, of varying the magnitude of the diffusion coefficient for a uniform membrane, of varying the diffusion coefficient across the membrane, and of excluding volumes to diffusion.

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PREFACE

The work described in this report was performed by the Guidance and Control Division of the Jet Propulsion Laboratory.

ACKNOWLEDGMENT

The general technique of the study presented here of using models and computer programs for electrochemical studies has been described by others. It follows from the direct adaption of the program CINDA-3G to the analysis of the observations from the physical and chemical characterization of GX separator material rather than from the use of modifications built upon other studies. I wish to thank Professor Phillip O'Brien, University of California at Los Angeles, for the adaption and general formulation of CINDA for use with these diffusion problems.

CONTENTS

TABLES

TABLES (contd)

FIGURES

CONTENTS (contd)

FIGURES (contd)

ABSTRACT

Models of diffusion across an inert membrane have been studied using the computer program CINDA. The models were constructed to simulate various conditions obtained in the consideration of the diffusion of Ag $(OH)_2^-$ ions in the AgO-Zn battery. The effects on concentrations across the membrane at the steady state and on the fluxout as a function of time were used to examine the consequences of stepwise reducing the number of sources of ions, of stepwise blocking the source and sink surfaces, of varying the magnitude of the diffusion coefficient for a uniform membrane, of varying the diffusion coefficient across the membrane, and of excluding volumes to diffusion.

SUMMARY AND CONCLUSIONS

The computer program CINDA has been used in a study of diffusion across membranes, such as battery separators. The procedure can be applied to selected problems when suitable models can be constructed to describe particular conditions. The results of the analyses, given in terms of concentrations at nodes for various designated time intervals and for the steady state and of outfluxes as functions of time, may be utilized to deduce the consequences of changing the properties of the membrane or the boundary conditions. Direct correlations of these analyses with definite membrane diffusion and battery data remain tenuous until the models can incorporate measurements of the physical properties of membranes, which in turn can be associated unequivocally with diffusion and battery performance.

With that caveat, the results of this study are summarized as follows:

VARIATION OF D FOR A UNIFORM MEMBRANE

Three levels of the diffusion coefficient (D) for a uniform membrane were used. The baseline value was 1×10^{-7} cm^2 sec^{-1}; the others were 3.6×10^{-9} and 6×10^{-11}. Increasing steady state concentrations were obtained with decreasing D. On the other hand, there were marked reductions in fluxout as a function of time with decreasing D; at the lowest D, no fluxout occurred during the 100 second interval. (A more complete determination of this dependence will be done using longer time units). The nature of the data emphasize the premise that the flux can be regulated.

VARIATION IN D ACROSS THE MEMBRANE

The particular model for non-uniform D resulted in decreases of the fluxout for all time intervals and in irregular steady state concentration profiles, which reflected to some extent the variation in D. The need to determine the constitution of the membrane by chemical and physical analyses for the purpose of relating membrane characteristics to diffusion properties is evident from these data.

SURFACES WITH D DIFFERENT FROM D IN THE BULK OF THE MEMBRANE

The use of surfaces with a diffusion constant 23 times that of the baseline uniform value caused increases in fluxout and decreases in the steady state concentrations. When the surface diffusion constant was 1/25 of the baseline value, the changes were much larger in the opposite direction. This result was shown to follow the mathematical consideration. The controlling of diffusion by surfaces with smaller D than the bulk was emphasized by these data.

REDUCTION IN THE NUMBER OF SOURCES

The stepwise decrease in the number of sources while maintaining fully permeable surfaces resulted in decreases in steady state concentrations at the sink surface whereas non-linear decreases occurred at the source. The spacial asymmetry introduced by the positioning of the sources caused non-uniform concentration profiles.

EXCLUSION OF SECTIONS OF SOURCE AND SINK SURFACES

At the steady state the sink surface concentrations increased with the reduction in the amount of surface, the increases being greater opposite the remaining sources. Non-uniform concentration profiles were caused by the spacial asymmetry. The fluxout was greater when the surfaces were blocked than for comparable cases when only the sources were reduced. Although these data were obtained for rather special, simple models, the results indicate that the consequence of the reduction of sources and the blocking of surfaces introduces considerable asymmetry and markedly affects the diffusion magnitude.

EXCLUSION OF VOLUMES WITHIN THE MEMBRANE

The exclusion of isolated volumes to diffusion caused a general increase in the steady state concentrations and marked decrease in fluxout, especially at the earliest times.

This study is illustrative of the types of diffusion problems which can be described by the computer program CINDA. Refinements in the modeling will be undertaken. Other parameters of the membrane and other boundary conditions can be used. For example, time dependent fluxes can be considered. It is believed that the data can be used to define the membrane characteristics required for particular membrane diffusion properties, thus limiting the range to sensible selection, and concurrently to delineate the range of operating conditions for desired diffusion properties for certain membranes.

DIFFUSION ACROSS THE MODIFIED POLYETHYLENE SEPARATOR GX IN THE HEAT-STERILIZABLE AgO-Zn BATTERY

INTRODUCTION

This study of the diffusion properties, which result from particular features of heterogeneous membranes, was undertaken in an effort to correlate the transport properties with the physical and chemical characteristics of the separator used in the heat-sterilizable AgO-Zn battery. The properties of this material which are dealt with here are not unique, and it is believed that other areas of membrane research, in which the consequences of heterogeneity must be considered, will contain analogous concerns. The situation of particular interest is one in which the membrane structure has been changed so that the membrane at the solution-membrane interface is not uniformly permeable. The analysis may be directly utilizable for investigations of instances of similar membrane heterogeneity.

The Heat Sterilizable Battery Program was formulated in response to the need to provide batteries capable of performing satisfactorily after being dry heat sterilized under the conditions required for the Mars Lander Mission, Voyager (see Appendix A). The sterilization procedure, devised to prevent the seeding of earth-life on planets by means of spore travel through interplanetary space, was changed several times during the period of the battery development in attempts to construct conditions correlating with the results of studies to determine the efficacy of various modes of sterilization. Since it was obviously ill-advised to readjust a development program for each change, a sterilization procedure, which was assumed to be the most severe of those which would probably be used as a final procedure, was utilized throughout the program; this was a heat soak at 135°C for 72 hours.

The development of a suitable AgO-Zn battery was the primary objective at the start of the program. (Subsequently, the development of a sterilizable NiO(OH) - Cd cell was added as a major effort, and this goal was successfully achieved). (See Ref. 1.) During the preliminary testing of available AgO-Zn batteries it was found that the heat-sterilization conditions caused severe decreases in performance, and it was shown that the separator was rapidly and catastrophically degraded. Indeed, the conclusion that the separator was often the limiting factor in determining the performance of AgO-Zn batteries, which had been established in many cases for non-sterilizable conditions, was demonstrated to be even more pertinent for heat-sterilization. It was apparent from these testing results that no usable sterilizable battery could be fabricated by including the commonly used cellulosic separator materials. Consequently, since the entire development depended upon this crucial item, intense efforts were undertaken to synthesize inert membranes having the proper physical, chemical, and electrochemical properties. These efforts included the synthesis of polyethylene grafted with acrylic acid; (Refs. 2 and 3) of poly-aliphatic-benzimidazoles, - benzoxazoles, and - benzothiazoles; (Ref. 4) of polymers of ethylene and acrylic acid; (Ref. 5) of composites containing zirconia bound with polysulfone to a polypropylene matrix; (Ref. 6) and of polymers composed of 2 - vinylpyridine, acrylic acid, styrene, and maleic acid (Ref. 7). Of these only the modified polyethylene had the properties requisite for use as a battery separator, and it was used throughout the cell and battery development program (Ref. 8).

The procedure for processing this polyethylene material (GX) was first developed by RAI Inc. (Ref. 2). However, the film which was used in the development of the heat-sterilizable AgO-Zn cells was produced by Southwest Research Institute (SWRI) (Ref. 3) employing the RAI method, as modified using irradiation and washing procedures developed by SWRI. A summary of some of the chemical and physical properties of the GX material is presented here, since, in part, it provides the basis for the undertaking of this study of the diffusion characteristics of non-uniform membranes. The GX material is described more fully in Refs. 9, 10, 11 and 12.

The GX separator was prepared from commercial 0.0025 cm thick Petrothane 301 (Phillips Petroleum Co.) and Dow 400 (Dow Chemical Co.) polyethylene films by first grafting chains of poly-(potassium acrylate) and then by crosslinking the acrylic acid chains with divinylbenzene, using irradiation from a Co^{60} source in each step. The swelling of the acrylate groups in the presence of concentrated aqueous KOH solution provides the pores and the environment for the transport of water, salts, and ions through the film. Crosslinking results in an increase in the capability to preserve an unchanged physical structure during heat-sterilization.

The processing causes an increase in the dry thickness to an average of 0.0050 cm; the thickness increases to an average of 0.0058 cm in 40% aqueous KOH solution. The nearly 50% crystallinity of the starting material remains essentially unchanged by the reactions, the acrylate being added to the amorphous volumes. It was shown that the hygroscopic properties are related to the type of counterion present. The greatest capacity for absorbing water is when K^+ ions are present, and this capacity decreases through the sequence of Na^+ - Li^+ - divalent ions; the film is not hygroscopic in the presence of divalent ions. A consequence of this difference in water absorption characteristics is that the film is flexible in KOH solution but is brittle in a solution containing a divalent ion, such as the Ca^{++} ion. This property is reversible.

For small samples taken from large sheets the acrylate concentrations varied from 8 to 50% by weight, the average being between 20 and 30% by weight per sheet. The acrylate concentration was also non-uniform across the film thickness, and a variety of cross-sectional concentration profiles was found: nearly constant, graded, and varying in a nearly symmetrical manner with distance from the surfaces, with either a maximum or a minimum near the center. These profiles became changed by reactions with solutions of 40% KOH or 40% KOH saturated with Ag_2O. In the latter instance depositions of mixture of Ag^o and Ag_2O also occurred. Although the experimental conditions used in the detailed study of these reactions were for long exposure times at 95°C and thus not directly comparable to the heat sterilization conditions, the observations of leaching and Ag^o deposition were similar for these two conditions when equivalent solutions were used. These results would seem to be descriptive of the consequences of years of stand-life of AgO-Zn batteries. Of course, leaching of PKA was accelerated during heat-sterilization.

The following concentration profiles of PKA were obtained as consequences of particular experimental conditions: (1) the loss of PKA as a result of a heat sterilization cycle yielded a constant concentration across the membrane. This condition was also obtained by very long exposure (3000 hours) at 95°C to a 45% KOH solution saturated with Ag_2O. (2) In contrast, exposure for a shorter time (1000 hours) under these conditions resulted in the nearly symmetrical variation of cross-sectional concentration with a maximum near the center and a concentration profile for Ag^o deposits which was qualitatively the reverse, i.e., there was a minimum near the center. Although the reduction to Ag^o occurs concurrently with the loss of PKA, the reactions do not occur at the same rate. It is assumed that the deposition of Ag species causes the clogging of volumes, which are normally swollen in the KOH solution, and consequently acts to emphasize the effects of the concomitant decrease in PKA concentration in decreasing the diffusion constant.

In a previous report (Ref. 13) an analysis was presented of one aspect of the transport characteristics of the $Ag(OH)_2^-$ ion in the AgO-Zn electrochemical cell. The system was taken to be that of a cell developed in the Heat Sterilizable Battery Program in which the electrolyte solution is a 40% aqueous KOH solution saturated with ZnO. It was assumed that the separator was homogeneous and inert to chemical attack. The transport of $Ag(OH)^-$ ions was taken as being by diffusion only. Using the Laplace transform method, equations were derived for the one dimensional case in which there is a source with a constant flux in at one surface and a sink with a constant flux out, not necessarily equal to the source-flux, at the other surface. These special conditions were described for the concentrations at the source and sink when times are so short that they act independently and when a very small current flows. Thus, the first report dealt with a simplified, ideal case.

CONSIDERATIONS OF HETEROGENEITY

In the first section of this present study the effects of several types of heterogeneity on the diffusion of $Ag(OH)_2^-$ ions across the GX separator were considered. The conditions of heterogeneity were derived directly from the results of studies of the reactions of this material, as cited above. The cases analyzed were restricted to the ones which were more directly relatable to the operation, performance, and problems of AgO-Zn batteries. They were:

Case 1. The membrane was assumed to have a constant diffusion coefficient for $Ag(OH)_2^-$ ions. This baseline case was used as a comparison. The faces were assumed to be uniformly permeable. This was intended to describe the data obtained for some sections of the unused, swollen GX separator material as well as for the condition of the material resulting from a heat sterilization cycle or from very long exposure to a 40% KOH solution saturated with Ag_2O.

Case 2. The membrane with uniformly permeable faces was assumed to have a diffusion constant which decreased with the distance from the center to each face. This was intended to be descriptive of the PKA concentration profile prevailing in some sections of the unused, swollen GX and in sections leached by moderately long exposure to the electrolyte solution of the AgO-Zn battery.

Case 3. The membrane was assumed to be homogeneous except for isolated permeable areas on the face next to the Ag electrode. This, in effect, is the case for an isolated source, which was used as a model for the situation which occurs in sections of a separator in a AgO-Zn cell in which the first deposition of Ag^o occurs in the segment of the separator wrap nearest the Ag electrodes. The deposition is observed to result from electrical cycling.

Case 4. The membrane was assumed to have a mixture of permeable volumes and excluded volumes. This condition can be obtained deliberately by precipitating inorganic compounds, such as MnO_2, throughout the permeable volume.

The types of heterogeneity of inert membranes considered in the second section were selected as being of a more general nature. Thus, the consequences may also be more generally correlatable with studies of diffusion in membrane systems other than those of battery separators. Specifically, the cases analysed here allow comparisons of the membrane for circumstances in which both surfaces become progressively clogged and thus non-permeable. In effect, this clogging is taken as being a process which results in the physical loss of particular spaces of the membrane surfaces to diffusion processes. It is assumed that this could be caused by a local degradation of the membrane surfaces either by complete loss of the entities which give rise to permeability or by the complete physical obstruction of the conditions which are favorable to diffusion, e.g., the disappearance of ion exchange sites or of moieties which cause the solvent-swelling of the membrane.

In one series of models the effects of progressively reducing the number of equal sized sources while maintaining the conditions of a uniform diffusion constant across the membrane and along the inside surfaces of the membrane were determined. In the case of the battery, the existence of isolated sources can be thought to be due to the physical positioning of the separator nearest to a spot of localized high electrode activity.

In a second series of models data were obtained for conditions of blocking off areas on both the source-and-sink surfaces and simultaneously reducing the number of sources; the condition of uniform diffusion constant was continued.

Finally, the models were used to describe the consequences of reducing the number of sources under the condition of a varying diffusion coefficient. Here the coefficient was taken as decreasing with the distance from the center to each surface.

METHOD OF ANALYSIS

The analyses were performed using the computer program CINDA-3G (Chrysler Improved Numerical Differencing Analyzer), which was designed for the solution of thermal analog models presented in a network format. The network representation allows a one-to-one correspondence to both the physical model and the mathematical model. This permits the quick construction of mathematical models of complex thermophysical problems. The extension of the procedure from the thermal analysis to the consideration of membrane diffusion problems was done using a lumped parameter representation of the membrane in which a network of concentration nodes was created. Each node was assigned a capacity equivalent to the volume encompassing the node. Conductors, with conductances calculated from the product of the diffusion constant and the cross-sectional area (through which the conductor passes) divided by the lengths of the conductor, were placed as connections between the neighboring nodes. A two dimensional representation was used taking equal volumes about the nodes in a manner such that 20 nodes spanned a 5.0×10^{-3} cm thick membrane, and there were 10 nodes in a direction parallel to the surfaces of the membranes. The different rates of influx were introduced at the surface or at isolated sources as moles of $Ag(OH)_2^-$ cm^{-2} sec^{-1}. These rates were derived from reasonable current densities for charging the AgO-Zn battery.

The formation and extension of the non-permeable spaces and the concurrent isolation of flux-sources-and-sinks were accomplished by setting the conductors leading to these blocked spaces equal to zero. An alternate procedure in which the volumes are set equal to zero is not permitted in using CINDA. The use of zero was arbitrary, since any value of these conductors, which was very small compared to the values for conductors connecting usable volumes, would have been sufficient to cause the blocking.

The non-uniform conductivities were obtained by using a model in which different diffusion coefficients were assigned to seven slabs sliced parallel to the surfaces. The center slab, which had the lowest value, was taken as the thickest one. The values used were: 1×10^{-8}, 3.2×10^{-8}, 1×10^{-7}, and 3.2×10^{-7} ($cm^2\ sec^{-1}$). These values can be compared with the diffusion constants reported for soluble Ag species in concentrated aqueous caustic solutions: in 10.1 M KOH (2.3×10^{-6}) (Ref. 14), in 10M Na OH (8.7×10^{-7}) (Ref. 15), and across the GX separator material in 40% KOH (5.2×10^{-8}, 3.5×10^{-9}, 2.3×10^{-8}) (Refs. 3, 16 and 17). The disparity in the coefficients for GX obtained in these studies is due to the use of different materials bearing the same generic name, although the wide ranges of values which were also reported for the same batch of GX were probably indicative of the non-uniform characteristics cited above.

It should be noted, however, that it is not correct to use any of these values directly as diffusion coefficients within the membrane. This follows from the realization that the values were determined using $J = -D(\Delta C/\Delta X)$, where J is the flux in moles $cm^{-2}\ sec^{-1}$, D is the diffusion constant in $cm^2\ sec^{-1}$, ΔC is the difference in bulk solution concentrations, and ΔX is the thickness of the membrane. Thus, the diffusion constants were calculated from measurements for the system of solution 1/membrane/solution 2. In such a composite system the applicable equation for steady state is

$$\frac{\Delta X_1}{D_1} + \frac{\Delta X_2}{D_2} + \frac{\Delta X_m}{D_m} = \frac{\Sigma \Delta X}{D}$$

where ΔX_1 and ΔX_2 are the thicknesses of the liquid surface layers for solutions 1 and 2, D_1 and D_2 are the respective surface diffusion coefficients,

X_m is the membrane thickness, D_m is the membrane diffusion coefficient, and D is the measured or apparent diffusion coefficient. There are techniques for the experimental determination of D_m (for example, Ref. 18). No attempts have been made in this study to calculate and to use values for D_m derived correctly from the experimentally determined apparent D values.

In each of these cases the membrane model system was characterized by determinations of the concentration profiles within the membrane at times for transient and steady state conditions and of the magnitudes of the flux (outflux) at a sink at various times. The fluxout was defined at the sink as the sum of the products of each conductor connected to the sink and the concentration of the node adjoining the sink minus the product of the sum of the conductors leading to the sink and the concentration of the sink. For example, in this case the sink at node 206 is connected to node 100 by connector 393, to 119 by 394, and to 140 by 395; and the equation is:

$$\begin{aligned}\text{fluxout} = {} & G(393) \cdot T(100) + G(394) \cdot T(119) + G(395) \cdot \\ & T(140) - [G(393) + G(394) + G(395)] \cdot T(206)\end{aligned}$$

In some cases the transient-concentrations were defined completely when the outfluxes at a designated sink were 5% and 90% of the influx at a particular source. However, in some instances the print-out of one or both of the sets of transients concentrations was not performed, the calculation being prevented by use of an artibrary time limitation on the computer calculation. These concentration profiles and the rates of influx and fluxout were used to compare the cases described above.

RESULTS AND DISCUSSION

The responses of the various models of the membrane have been examined by comparing the time dependence of the fluxout at one node on the sink surface; the concentration profiles across the membrane for the conditions of steady state and when the ratios of the (influx-fluxout)/influx were 0.95 and 0.10, whenever these data were available; and the concentration profiles along the source and sink surfaces. Some comparisons were precluded by the limitations resulting from the conditions imposed on the models and from the time alloted for the transient analyses, the maximum transient time having elapsed before a programmed calculation could be done. The calculations for the steady states, were performed in each case, however, since in the computer computation the solution of Poisson's equation was utilized for steady state analyses.

VARIATION OF DIFFUSION COEFFICIENT

The effect of the magnitude of the membrane diffusion coefficient was determined by assigning three different values to the coefficient for a model of uniform properties. The effect of a varying coefficient was also described, using the model of slabs cited above. The values used for the cases of a uniform membrane were 1×10^{-7}, 3.6×10^{-9}, and 6×10^{-11} (cm^2 sec^{-1}). Two influxes were use: 2.5×10^{-15} and 7.5×10^{-14} (moles sec^{-1}). These fluxes correspond approximately to current densities of 4 and 120 ma cm^{-2}, rather wide limits for the charging current of Ag electrodes.

The consequences of these particular variations of the diffusion coefficient on the concentrations across the membrane for the steady state condition can be illustrated using the data given in Table 1. These data are for full surfaces of sources and sinks. A general conclusion is that the concentration at a particular mode increases with decreasing values for the diffusion coefficient. If the consideration is limited to $Ag(OH)_2^-$, or to other ions with nearly the same "solubility" and diffusion coefficient, then all the steady state concentrations in the membrane, as shown in Table 1, exceed the solubility limit.

The effect of the magnitude of the diffusion coefficient on the output at one sink for the case of full surfaces of sources and sinks is indicated by the data given in Table 2. It is evident that the particular set of coefficients used to make up the varying diffusion constant, as cited above, causes a diminution of the outflux at a particular time when compared with the baseline constant coefficient, 1×10^{-7} cm^2 sec^{-1}. The effects of decreasing the coefficient, for the cases of uniform diffusion, to the values of 3.6×10^{-9} and 6×10^{-11} cm^2 sec^{-1} are very large; thus, the decrease by 3.6×10^{-2} in the first instance results in no outflux for the first 45 seconds, and the first outflux at 50 seconds is 4×10^{-14} times the baseline value. However, the ratio of these outfluxes decreases to 5×10^{-8} at the 100 second point. Obviously, the data for $D = 6 \times 10^{-11}$ cm^2 sec^{-1} reveal that this further change in the diffusion coefficient results in zero outflow during the 100 second period.

Some further comparisons for a constant D = 1×10^{-7} and the case of varying D are discernible from the data described in Figures 1, 2, and 3. In Figure 1 the comparison is of the outflux vs time for these two cases. In Figures 2 and 3 the steady state concentrations are compared for two influxes. The irregular curves for the non-constant D contrast with the smooth for constant D.

INFLUENCES OF SOURCES AND SURFACES

Two general models for decreasing the numbers of sources and sinks have been used. In one the number of sources is decreased stepwise while maintaining diffusion paths along the surfaces. In the other the stepwise decrease of the number of sources is accompanied by the stepwise blocking of sections of the surfaces to diffusion, i.e., as if parts of the surface are blocked or clogged by a precipitate. In these particular models, the blocking of a section of the surface is equivalent to excluding sources from that section; this was done by giving the value of zero to all conductors leading from the blocked section. These two general models are intended to describe two conditions obtainable in an electrochemical cell. In the first case the various conditions of decreased permeable area of the membrane surface is assumed to result from the juxtaposition of isolated active areas of the electrode and the separator. In the second case the various situations are assumed to be obtained by the deposition of solids in the surface layers of the separator.

The data have been examined within the context of the responses of the model to the imposition of three variables: the number of sources, the amounts of permeable source-and-sink-surfaces, and a conductivity variation. Comparisons were made of the effects of these variations on the times to reach the 95% transient stage, the concentration differences across the membrane at the 95% stage and at steady state, the concentration differences along the sink surface, and the magnitude of the outflux as a function of time.

In the first set of data the conditions of uniform conductivity (uniform diffusion coefficient and evenly spaced modes) and fully permeable surfaces were maintained. The number of sources was reduced stepwise in the sequence 10, 6, 3, 1. Some data are shown in Table 3. These general trends are apparent: (1) at the 95% stage the concentrations at the sink surface were little changed by variations at the source surface of 3.3 to 1, and the times needed to reach this stage increased with the reduction in sources. (2) At the steady state the decreases in concentrations at the sink surface follow directly proportional to the number of sources whereas simultaneously non-linear decreases occur at the source.

The variations in the concentration profiles at the steady state as a function of the stepwise reduction in sources, maintaining full surface permeability, are also shown in Figure 4. Since these data are for one line of nodes perpendicular to the surfaces, a non uniformity of concentrations results from spacial asymmetry. Thus, for ratios of the sources of 1.67, 3.33, and 10 the concentration ratios at the source surface are 2.14, 4.1, and 6.65 and the concentration ratios at the sink surface are 3.0, 5.9, and 10.

The effects on concentration asymmetry of using a single isolated source with full surface permeability are shown in Figure 5, where the data are for the steady state. The top curve is the concentration profile which contains the node with the isolated source.

The consequences of the dependence of outflux on time going from a full surface of 10 sources to an isolated source are shown in Figure 6. The outflux is directly proportional to the number of sources at each time interval.

In the second set of data the condition of uniform conductivity was maintained, and the effects of decreasing the number of sources at each step of the process of progressively decreasing the available surfaces were determined. Some data are given in Table 4. These general trends are apparent: (1) At the 95% stage for each group at a constant decreased surface the concentrations at the sink surface varied along the surface depending on the positions relative to the sources, the sink opposite the source being higher. The reduction to a single source and sink together with the simultaneous blocking of both surfaces except for these positions resulted in aberration such that an increase occurred at the sink opposite the source while the source decreased. The times required to reach the 95% stage decreased with the decreasing amount of surfaces. The concentration profiles shown in Figure 7 illustrate the effects of an isolated source and an isolated sink, which are not placed colinear perpendicular to the surfaces. (2) At the steady state the effects of the surface reductions are marked, the sink concentrations increasing with surface reduction. The increases are greater opposite the remaining sources. Although there are increases of about 11-fold at a sink opposite a source, the concentration at that source changes less rapidly over a span of 1.33 fold.

The steady state concentration profiles in Figure 8 show the asymmetric effects of an isolated source and an isolated sink, which are not placed colinear perpendicular to the surfaces. When these differences are compared with those given in Figure 7 at the 95% stage, it is seen that, in general, the relative positions of the curves in the two sets differ only in magnitude.

In Figure 9 a comparison is made of two types of isolated sources. In one the full surfaces of sources and sinks are permeable. In the other the surfaces are blocked with the exception of one source and one sink. It is apparent that the consequence of closure of the source surface is to markedly increase the concentration at the source surface while the open sink surface depresses the concentration at that surface.

The effect of surface blocking on the time dependence of the fluxout is shown in Figure 10. The top curve is for the condition of full source and sink surfaces. A comparison of the other two curves shows that the blocking of the surfaces except for a single source and a single sink causes outfluxes greater than for the case of a single source with unblocked surfaces, the differences diverging with time. As noted above, the outflux is measured at one sink. Consequently, whereas this comparison is valid for the consideration of outflux at that sink, it is apparent that a comparison of the total outflux through the sink surface of the model is in effect given by using the curve for the full surface.

Data describing the effects of imposing a varying conductivity onto the stepwise decrease of the number of sources while maintaining fully permeable surfaces are given in Tables 5 and 6. These results are noted: (1) At the 95% stage for a full surface of source and the lower flux rate of 2.5×10^{-15} moles sec^{-1}, 2.4 times as much time is used for the graded diffusion coefficient; and the concentrations at the source and at the sink surface increased by 4- and 10-fold, respectively. At the higher rate of 7.5×10^{-14} moles sec^{-1}, the same time ratio occurred while the concentration ratios at the source and sink were nearly constant at 3.7 and 10, although the overall concentrations for the 30-fold increase in flux increased by nearly exactly

30-fold. (2) At the 95% stage for an isolated source and the lower flux rate, the concentrations at the source and sink both increased by 5-fold for the graded case. The use of the higher flux caused the same ratio of increase, although the overall concentrations again varied by 30-fold. (3) At the steady state for the lower flux and full surface of sources the change of conductivity caused the concentrations at the source and sink to increase by 2.4-fold and 3.2-fold, respectively. On the other hand for the isolated source at the lower flux this change caused the ratio for the sources to vary by 4.3 while the sink ratio remained at 3.2-fold despite a 10-fold decrease in overall concentration as a result of the isolated source. At the higher flux and full source-surface the conductivity change resulted in increases of 2.2- and 2.0-fold at the source and sink, respectively. In the case for the isolated source these ratios were 4.3 and 3.2, respectively. The steady states at the higher flux were the same as the 95% stage.

The determination of the effects engendered in models, which were constructed so that the surface layers had diffusion coefficients which differed from the value of the uniform body of the membrane, was done for two cases. The surfaces were limited to the first and last columns of nodes, and the values used were 4×10^{-9} and 2.3×10^{-6} cm^2 sec^{-1}. The changes in outflux as a function of time and of the concentration profiles at the steady state were compared. These data are given in Table 7 and 8 and Figures 11 and 12.

That the substitution of surfaces with a diffusion coefficient of 23 times the magnitude of the uniform value has yielded discernible increases in outflux and decreases in concentration throughout the membrane cross section is apparent from these data. However, the effects of the use of surfaces with a diffusion coefficient of 1/25 of the uniform value clearly results in markedly greater differences in the opposite direction. For the steady state this distinction can be deduced by considering that at the steady state the flux is a constant through each surface that separates two phases, such as the surface and the bulk of the membrane in this case. Using J as the common flux, D_s, D_b, and D_a are the surface, bulk; and apparent diffusion coefficients, respectively, and ΔX are the thickness of a node, the equation is

$$\frac{2J \cdot \Delta X}{D_s} + \frac{16\, J \cdot \Delta X}{D_b} = \frac{18\, J \cdot \Delta X}{D_a}$$

The two models can be compared by setting $D_s = 23\ D_b$ in one case and $D_s = D_b/25$ in the other case. Thus, for $D_s = 23\ D_b$

$$\frac{2}{23\ D_b} + \frac{16}{D_b} = \frac{18}{D_a} \text{ and } D_a = 1.12\ D_b$$

For $D_s = D_b/25$, $\frac{50}{D_b} + \frac{16}{D_b} = \frac{18}{D_a}$ and $D_a = 0.273\ D_b$. The much greater effect obtained by decreasing the surface diffusion coefficient is evident.

INFLUENCE OF EXCLUDED VOLUMES

The simulation of membranes having excluded volumes throughout, as may be the case for battery separators for which one step of the preparation is the precipitation of $Mn\,O_2$ within the material, was done by excluding nodes from diffusion. These nodes were distributed in a regular pattern throughout the 10×20 node model. There were 39 excluded nodes out of the total 200 nodes. The data for examining the effects of this model are given in Tables 9 and 10 and in Figures 13, 14, 15, and 16.

From the data for the steady state it is evident that the effect of excluded volumes is similar to that for decreasing the diffusion coefficient, since in general the concentrations for the excluded volumes-model are higher than their counterparts for both full surface and isolated sources. A reversal of this relation occurs in the case of the full surface source at the point 2/3 from the source surface to the sink surface. This reversal does not occur in the case of an isolated source. This feature of the concentration profiles at the steady state remains inexplicable.

The marked decreased in outflux as a consequence of the excluded volumes are apparent in the data for outflux as a function of time. As was the case for decreasing the diffusion coefficient, the depression of the outflux is greatest at the earliest times.

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APPENDIX A

The battery technology goals for Voyager were established for three types of batteries: A primary/hard lander, a primary/soft lander, and a secondary/soft lander. The goals for the primary/hard lander battery were: (1) a capacity of 600 watt hours at an energy density of at least 55 watt hours/kg; (2) an output voltage at rated load of 22.5 to 33.5 vdc; (3) a capability of supplying a 300 watt load at rated voltage; (4) a capability of being discharged and charged at 100% of the rated capacity at least four times after heat sterilization; (5) a capability of a 9 month storage period in the charged state after sterilization; and (6) a capability of operating satisfactorily after an impact shock of 2,800 ± 200 g at 35.1 ± 0.9 m/sec. The goals for the primary/soft lander were similar with the exceptions of: (1) a capacity of 2000 watt hours at an energy density of at least 77 watt hours/kg; (2) a capability of supplying a 500 watt load at rated voltage; and (3) the elimination of the high impact requirement. The goals for the secondary/soft lander battery which differed from the primary/soft lander battery were: (1) a capacity of 1200 watt hours; (2) a capability of 400 discharge-charge cycles to 50% of rated capacity; and (3) capability of supplying a 200 watt load at rated voltage.

A brief summary of the results of this battery development is extracted from the final report for this program. (The complete description is given in "Heat Sterilizable Impact Resistant Cell Development," Final Report on JPL Contract 951296, October 1, 1967, to September 1, 1971, by ESB, Incorporated).

The 25 AH, high shock cells were shown to be capable of a cycle life of 72 to 121 cycles under the regime of a 10 hr charge and a 2 hr discharge to a 50% level. (All of these data refer to after heat sterilization). Energy densities of 47.4 WH/kg and 0.1 WH/cm^3 at a C/2 rate were obtained for the cells. Engineering models survived peak shock loads of 4000 g in all axes except for the terminals-forward position.

The 5 AH, high shock cells had energy densities of 23.3 WH/kg and 0.06 WH/cm^3. These cells withstood peak shock loads of 4000 g from 36.6 m/sec in all axes. Batteries fabricated from these cells for the Capsule System Advanced Development (CSAD) Project performed satisfactorily after being drop tested and sustaining shocks in the range of 1300 to 2400 g.

A primary 70 AH cell yielded mean energy densities of 117 WH/kg and 0.23 WH/cm^3 when discharged at the C/4 rate. These cells delivered 16 cycles during a wet life of 16 months.

A 25 AH Low Impact, Intermediate Cycle Life Cell gave up to 168 cycles over a 9.5 month wet life in a regime of 10 hr charge and a 2 hr discharge. The energy densities of the sealed cells were 97 WH/kg and 0.16 WH/cm^3.

The 20 AH Low Impact, High Cycle Life Cell yielded 241 cycles on a 20 2/3 hr charge and a 3 1/3 hr discharge cycle. The energy densities were 66 WH/kg and 0.11 WH/cm^3 for the cell.

Table 1. Steady State Concentrations Effects of Diffusion Coefficients

(Full Surfaces)

	J =	2.5×10^{-15}				7.5×10^{-14}		
	D =	1×10^{-7}	3.6×10^{-9}	6×10^{-11}	Variable	1×10^{-7}	3.6×10^{-9}	6×10^{-11}
Node		(1)	(2)	(3)	(1)	(2)	(3)	(4)
21		1.43	1.60	8.51	3.50	4.30	4.79	2.55
22		1.34	1.35	7.07	2.50	4.01	4.06	2.12
23		1.24	1.14	5.81	1.51	3.73	3.41	1.74
24		1.15	0.946	4.72	1.20	3.45	2.84	1.42
25		1.06	0.789	3.78	0.888	3.19	2.34	1.13
26		0.977	0.635	3.00	0.794	2.93	1.90	0.899
27		0.894	0.512	2.34	0.702	2.68	1.54	0.702
28		0.814	0.409	1.80	0.675	2.44	1.23	0.541
29		0.736	0.323	1.37	0.651	2.21	0.968	0.412
30		0.661	0.252	1.03	0.631	1.98	0.756	0.309
31		0.589	0.194	0.761	0.612	1.77	0.583	0.228
32		0.518	0.148	0.554	0.597	1.55	0.444	0.166
33		0.449	0.111	0.397	0.584	1.35	0.334	0.119
34		0.382	0.0823	0.280	0.574	1.14	0.247	0.0840
35		0.316	0.0598	0.194	0.549	0.947	0.179	0.0580
36		0.251	0.0423	0.131	0.527	0.753	0.127	0.0392
37		0.187	0.0286	0.0844	0.460	0.562	0.0857	0.0252
38		0.125	0.0176	0.0502	0.397	0.374	0.0528	0.0150
39		0.0622	0.00837	0.0233	0.197	0.186	0.0251	0.00699

Notes:

D in $cm^2 \; sec^{-1}$

J in moles sec^{-1}

(1) multiply by 10^{-3}

(2) multiply by 10^{-2}

(3) multiply by 10^{-1}

(4) multiply by 10

Concentrations in moles cm^{-3}

Solubility Ag_2O in 10m KOH is $4. 10^{-4}$m

Table 2. Effect of D on Outflux

(Full Surfaces)

	J=	2.5×10^{-15}				7.5×10^{-14}		
	D=	1×10^{-7}	3.6×10^{-9}	6×10^{-11}	Variable	1×10^{-7}	3.6×10^{-9}	6×10^{-11}
Time (sec)		(1)	(1)	(1)	(1)	(1)	(1)	(1)
5		0.290-20	0.000	0.000	0.158-22	0.872-19	0.000	0.000
10		0.269-17	0.000	0.000	0.163-19	0.806-16	0.000	0.000
15		0.242-16	0.000	0.000	0.343-18	0.726-15	0.000	0.000
20		0.740-16	0.000	0.000	0.198-17	0.222-14	0.000	0.000
25		0.147-15	0.000	0.000	0.627-17	0.440-14	0.000	0.000
30		0.234-15	0.000	0.000	0.142-16	0.701-14	0.000	0.000
35		0.328-15	0.000	0.000	0.260-16	0.984-14	0.000	0.000
40		0.425-15	0.000	0.000	0.417-16	0.128-13	0.000	0.000
45		0.522-15	0.000	0.000	0.608-16	0.157-13	0.000	0.000
50		0.617-15	0.263-30	0.000	0.828-16	0.185-13	0.789-29	0.000
55		0.710-15	0.298-28	0.000	0.107-15	0.213-13	0.894-27	0.000
60		0.798-15	0.688-27	0.000	0.134-15	0.240-13	0.206-25	0.000
65		0.883-15	0.764-26	0.000	0.162-15	0.265-13	0.229-24	0.000
70		0.965-15	0.540-25	0.000	0.191-15	0.289-13	0.162-23	0.000
75		0.104-14	0.278-24	0.000	0.221-15	0.313-13	0.834-23	0.000
80		0.112-14	0.113-23	0.000	0.251-15	0.335-13	0.340-22	0.000
85		0.119-14	0.385-23	0.000	0.283-15	0.357-13	0.115-21	0.000
90		0.125-14	0.112-22	0.000	0.314-15	0.376-13	0.339-21	0.000
95		0.132-14	0.295-22	0.000	0.345-15	0.395-13	0.886-21	0.000
100		0.138-14	0.699-22	0.000	0.377-15	0.413-13	0.210-20	0.000

D in $cm^2 \ sec^{-1}$

J in moles sec^{-1}

(1) Notation: For example, 0.290-20 ≡ 0.290×10^{-20} moles sec^{-1}

Table 3. Effect of Reduction in Number of Sources (Full Surfaces) on Concentrations at Sink Surface

	Sources =	10	6	3	1
95%	Sink 1	4.06-06	4.04-06	4.06-06	4.09-06
	Sink 2	4.06-06	4.04-06	4.03-06	4.00-06
	Source	6.21-04	4.16-04	2.70-04	1.86-04
	Time	2.21+01	2.63+01	3.54+01	7.25+01
Steady State					
	Sink 1	6.22-05	3.73-05	1.87-05	6.29-06
	Sink 2	6.21-05	3.73-05	1.86-05	6.20-06
	Source	1.43-03	8.67-04	4.61-04	2.14-04

Time is in seconds (e.g. 2.21+01 = 22.1 sec.)

Concentrations are moles cm^{-3} (e.g. 4.06-06 = 4.06×10^{-6} moles cm^{-3})

$D = 1 \times 10^{-7}$ cm^2 sec^{-1}
$J = 2.5 \times 10^{-15}$ moles sec^{-1}
Separation of Sink 1 and Sink 2 = 4 nodes
Source Opposite Sink

Table 4. Effect of Number of Sources and Blocked Surfaces on Concentrations at Sink Surface

	Surface Left =	0.6	0.6	0.6	0.3	0.3	0.1
	Sources =	6	3	1	3	1	1
95%							
	Sink 1	3.13-06	3.13-06	3.24-06	2.55-06	2.71-06	2.89-06
	Sink 2	3.00-06	2.97-06	2.96-06	1.96-06	1.91-06	1.58-06
	Source	4.42-04	2.70-04	2.07-04	3.05-04	2.46-04	2.38-04
	Time	2.25+01	2.89+01	5.14+01	2.30+01	3.52+01	2.84+01
Steady State							
	Sink 1	4.51-05	2.26-05	7.62-06	3.75-05	1.27-05	3.26-05
	Sink 2	4.28-05	2.14-05	7.11-06	2.76-05	9.17-06	1.77-05
	Source	9.32-04	4.87-04	2.54-04	5.51-04	3.11-04	3.17-04

Time is in seconds (e.g. 2.21 + 01 = 22.1 sec.)

Concentrations are moles cm^{-3} (e.g. 4.06-06 = 4.06×10^{-6} moles cm^{-3})

$D = 1 \times 10^{-7}\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$
Separation of Sink 1 and Sink 2 = 4 Nodes
Source Opposite Sink
$J = 2.5 \times 10^{-15}$ moles sec^{-1}

Table 5. Effects of Non-Uniform D and Number of Sources on Concentrations at Sink Surface ($J = 2.5 \times 10^{-15}$ moles sec^{-1})

		Uniform D		Non-Uniform D	
	Sources =	10	1	10	1
95%	Sink 1	4.06-06	4.09-06	4.00-05	1.99-05
	Sink 2	4.06-06	4.00-06	4.00-05	1.97-05
	Source	6.21-04	1.86-04	2.48-03	9.24-04
	Time	2.21+01	7.25+01	5.36+01	1.00+02
Steady State					
	Sink 1	6.22-05	6.29-06	1.97-04	1.99-05
	Sink 2	6.21-05	6.20-06	1.97-04	1.97-05
	Source	1.43-03	2.14-04	3.50-03	9.24-04

Time is in seconds (e.g. 2.21+01 = 22.1 sec.)
Concentrations are moles cm^{-3} (e.g. 4.06-06 = 4.06×10^{-6} moles cm^{-3})

Note: 95% and steady state are same for non-uniform D - isolated source

$J = 2.5 \times 10^{-15}$ moles sec^{-1}
Separation of Sink 1 from Sink 2 = 4 Nodes
Source Opposite Sink
Uniform $D = 1 \times 10^{-7}$ cm^2 sec^{-1}

Table 6. Effects of Non-Uniform D and Number of Sources on Concentrations at Sink Surfaces (J = 7.5×10^{-14} moles sec^{-1})

		Uniform D		Non-Uniform D	
	Sources =	10	1	10	1
95%					
	Sink 1	1.22-04	1.20-04	1.20-03	5.97-04
	Sink 2	1.19-04	1.23-04	1.20-03	5.97-04
	Source	1.56-02	5.59-03	5.79-02	2.77-02
	Time	2.28+01	7.25+01	5.57+01	1.00+02
Steady State					
	Sink 1	1.68-03	1.89-04	5.33-03	5.97-04
	Sink 2	1.68-03	1.86-03	5.32-03	5.91-04
	Source	3.72-02	6.42-03	8.39-02	2.77-02

Time is in seconds (e.g. 2.21+01 = 2.21 sec.)

Concentrations are moles cm^{-3} (e.g. 4.06-06 = 4.06×10^{-6} moles cm^{-3})

Note: 95% and steady state are same for non-uniform D - isolated source

J = 7.5×10^{-14} moles sec^{-1}
Separation of Sink 1 from Sink 2 = 4 Nodes
Source Opposite Sink
Uniform D = 1×10^{-7} cm^2 sec^{-1}

Table 7. Effect of Surface Diffusion Coefficient on Fluxout

Time (Sec)	$D_s = 1 \times 10^{-7}$	$D_s = 4 \times 10^{-9}$	$D_s = 2.3 \times 10^{-6}$
5	2.91-21	1.14-23	4.93-20
10	2.69-18	3.50-20	6.26-18
15	2.42-17	6.16-19	3.97-17
20	7.40-17	2.95-18	1.05-16
25	1.47-16	8.14-18	1.94-16
30	2.34-16	1.67-17	2.96-16
35	3.28-16	2.88-17	4.02-16
40	4.25-16	4.43-17	5.09-16
45	5.22-16	6.26-17	6.65-16
50	6.17-16	8.35-17	7.16-16
55	7.10-16	1.06-16	8.14-16
60	7.98-16	1.31-16	9.06-16
65	8.83-16	1.57-16	9.95-16
70	9.65-16	1.84-16	1.08-15
75	1.04-15	2.11-16	1.16-15
80	1.12-15	2.39-16	1.23-15
85	1.19-15	2.68-16	1.30-15
90	1.25-15	2.96-16	1.37-15
95	1.32-15	3.25-16	1.43-15
100	1.38-15	3.54-16	1.49-15

D in $cm^2\ sec^{-1}$

Fluxout in moles sec^{-1}

$J = 2.5 \times 10^{-15}$ moles sec^{-1}

Table 8. Effect of Surface Diffusion Coefficient on Steady State Concentrations

	$D = 1 \times 10^{-7}$	$D = 4 \times 10^{-9}$	$D = 2.3 \times 10^{-6}$
Node	(1)	(1)	(1)
24	1.43	3.77	1.27
22	1.34	1.35	1.26
23	1.24	1.26	1.18
24	1.15	1.17	1.09
25	1.06	1.09	1.01
26	0.977	1.01	0.933
27	0.894	0.942	0.854
28	0.814	0.876	0.776
29	0.736	0.815	0.700
30	0.661	0.759	0.625
31	0.589	0.707	0.552
32	0.518	0.662	0.480
33	0.449	0.620	0.409
34	0.382	0.582	0.339
35	0.316	0.549	0.270
36	0.251	0.520	0.202
37	0.187	0.495	0.134
38	0.125	0.474	0.0671
39	0.0622	0.181	0.0643

D is in $cm^2\ sec^{-1}$

(1) $\times 10^{-3}$ moles cm^{-3}

$J = 2.5 \times 10^{-15}$ moles sec^{-1}

Table 9. Effect of Excluded Volumes on Fluxout

	Uniform D		Excluded Volumes	
J =	Full Surface	Isolated Source	Full Surface	Isolated Source
Time (sec)				
5	2.91-21	1.90-22	- - -	- - -
10	2.69-18	2.44-19	- - -	- - -
15	2.42-17	2.31-18	3.48-29	5.05-30
20	7.40-17	7.19-18	4.19-25	2.96-26
25	1.47-16	1.44-17	4.09-23	2.99-24
30	2.34-16	2.31-17	7.41-22	5.90-23
35	3.28-16	3.25-17	5.69-21	4.88-22
40	4.25-16	4.22-17	2.61-20	2.39-21
45	5.22-16	5.19-17	8.58-20	8.25-21
50	6.17-16	6.14-17	2.23-19	2.24-20
55	7.10-16	7.06-17	4.92-19	5.10-20
60	7.98-16	7.95-17	9.53-19	1.02-19
65	8.83-16	8.80-17	1.67-18	1.83-19
70	9.65-16	9.61-17	2.73-18	3.05-19
75	1.04-15	1.04-16	4.17-18	4.75-19
80	1.12-15	1.11-16	6.06-18	7.02-19
85	1.19-15	1.18-16	8.46-18	9.93-19
90	1.25-15	1.25-16	1.14-17	1.35-18
95	1.32-15	1.31-16	1.49-17	1.79-18
100	1.38-15	1.37-16	1.90-17	2.31-18

Fluxout in moles sec^{-1}

Notation: Example, 2.91-21 $\equiv$ 2.91 10^{-21}

J = 2.5×10^{-15} moles sec^{-1}

Full Surfaces

Table 10. Effect of Excluded Volumes on Steady State Concentrations

	Uniform		Blocked	
	Full Surface	Isolated Source	Full Surface	Isolated Source
Node	(1)	(2)	(1)	(1)
21	1.43	2.14	4.82	1.20
22	1.34	1.74	4.04	0.894
23	1.24	1.51	3.51	0.743
24	1.15	1.34	3.12	0.618
25	1.06	1.20		
26	0.977	1.07	2.06	0.365
27	0.894	0.963	1.74	0.298
28	0.814	0.864	1.42	0.236
29	0.736	0.773	1.19	0.195
30	0.661	0.688	1.03	0.165
31	0.589	0.608		
32	0.518	0.532	6.17	0.0945
33	0.449	0.459	0.497	0.0751
34	0.382	0.389	0.379	0.0566
35	0.316	0.321	0.297	0.0442
36	0.251	0.255	0.240	0.0354
37	0.187	0.190		
38	0.125	0.126	0.0921	0.0134
39	0.0622	0.0629	0.0460	0.00666

$J = 2.5 \times 10^{-15}$ moles $\sec^{-1}$ NOTE: Concentrations in moles cm^{-3}

(1) Multiply by 10^{-3}

(2) Multiply by 10^{-4}

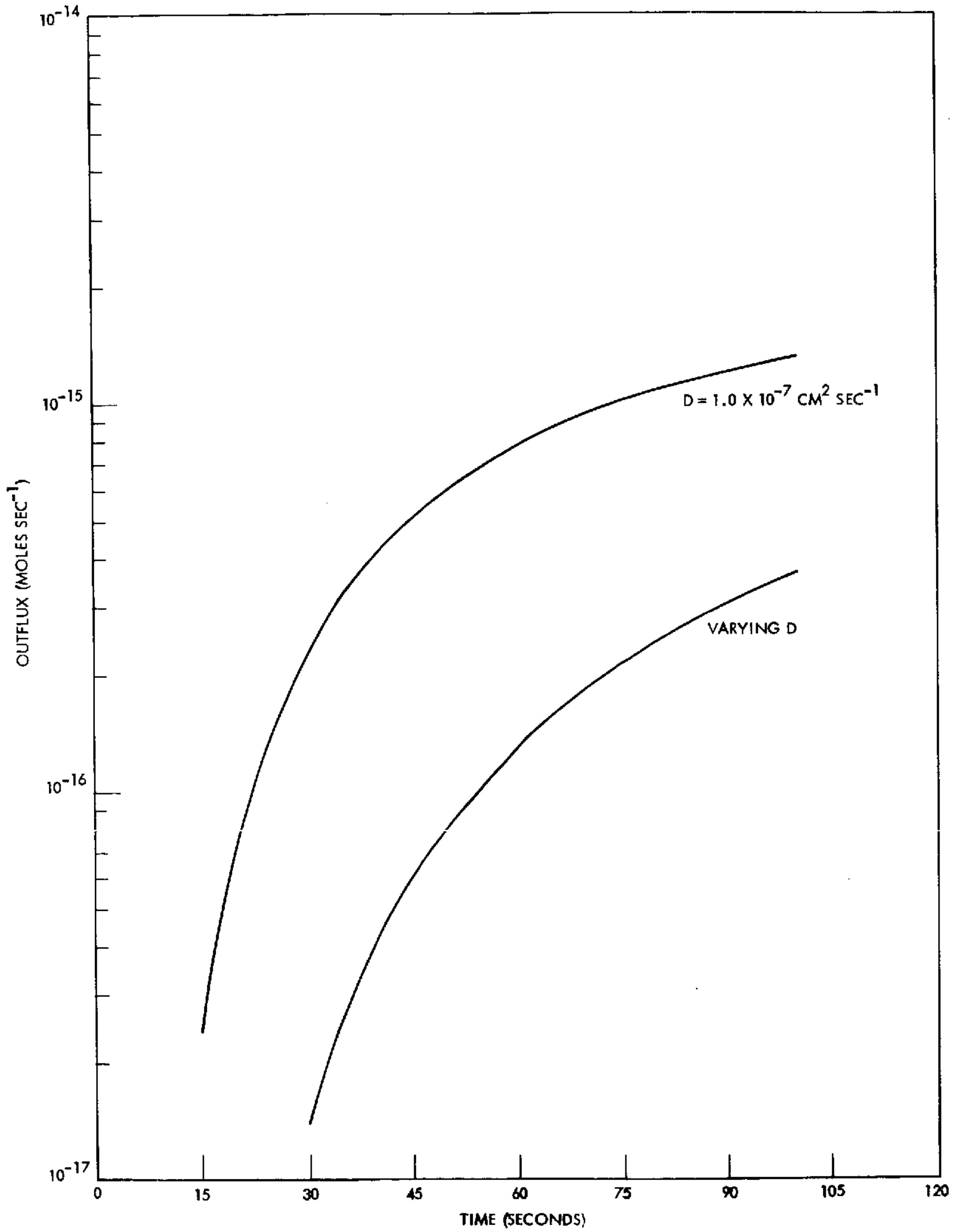

Figure 1. Effect of Varying D on Outflux

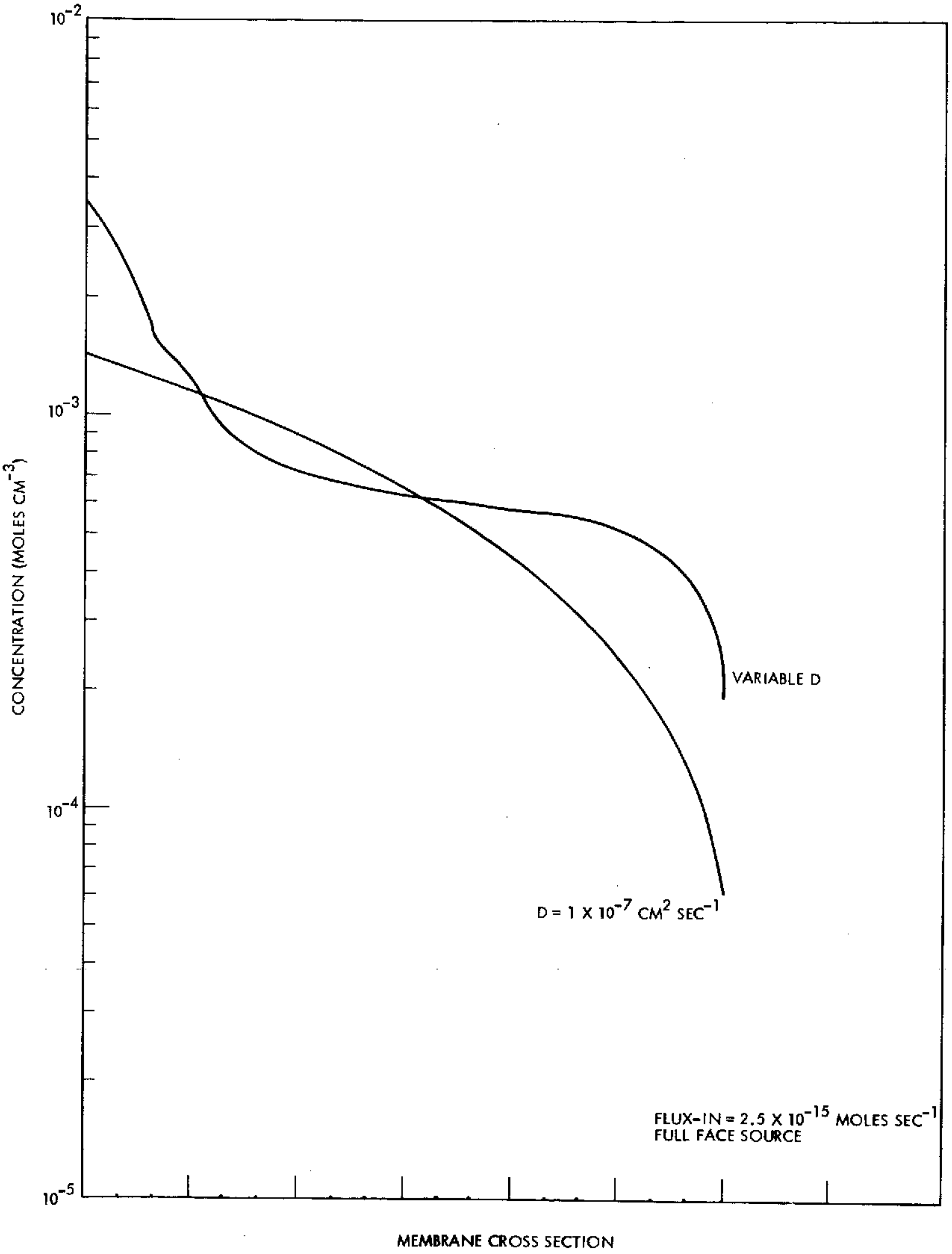

Figure 2. Effect of Varying D on Steady State Concentrations (Flux = 2.5×10^{-15} moles sec^{-1})

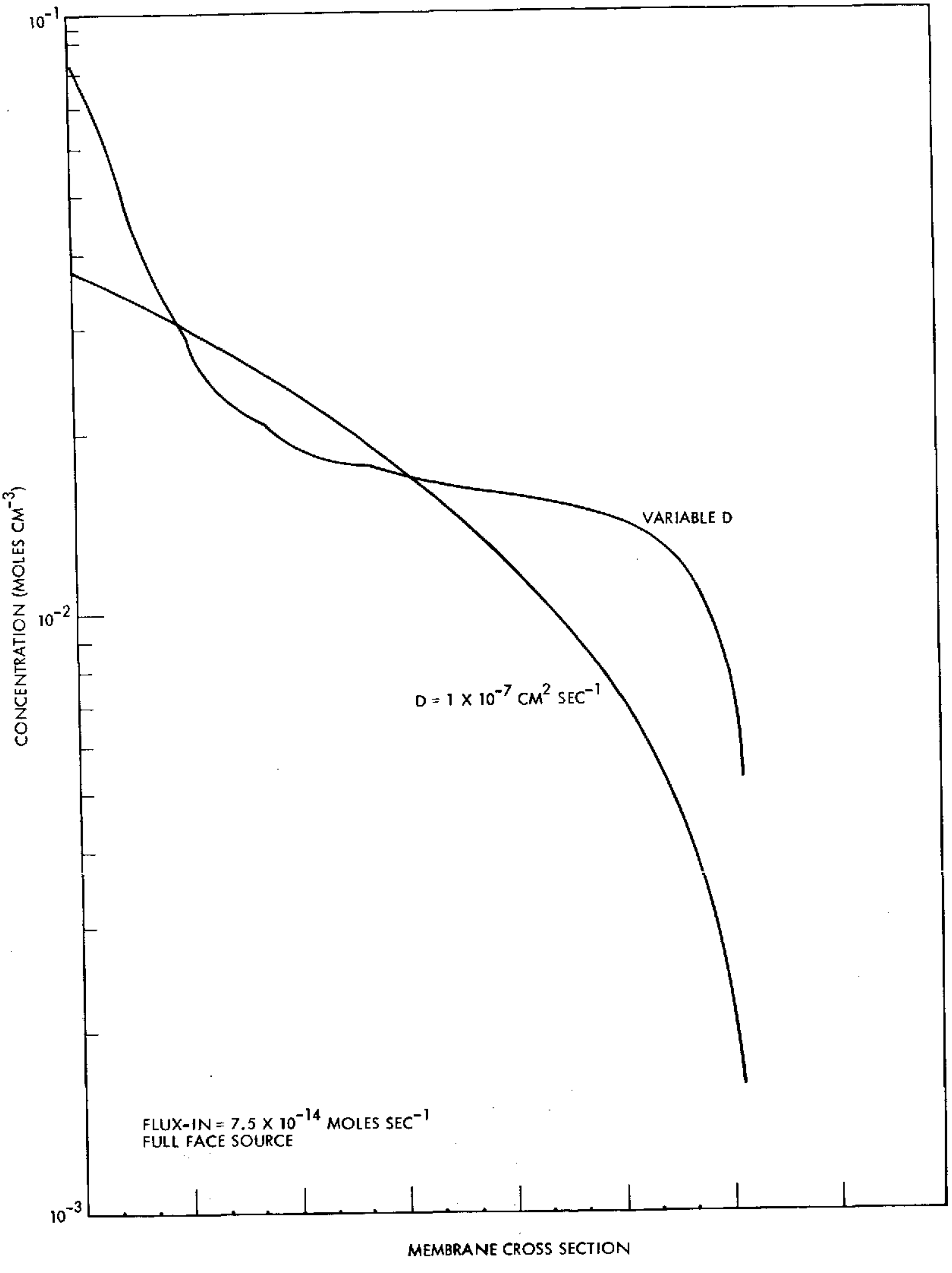

Figure 3. Effect of Varying D on Steady State Concentrations (Flux = 7.5 × 10^{-14} moles sec^{-1})

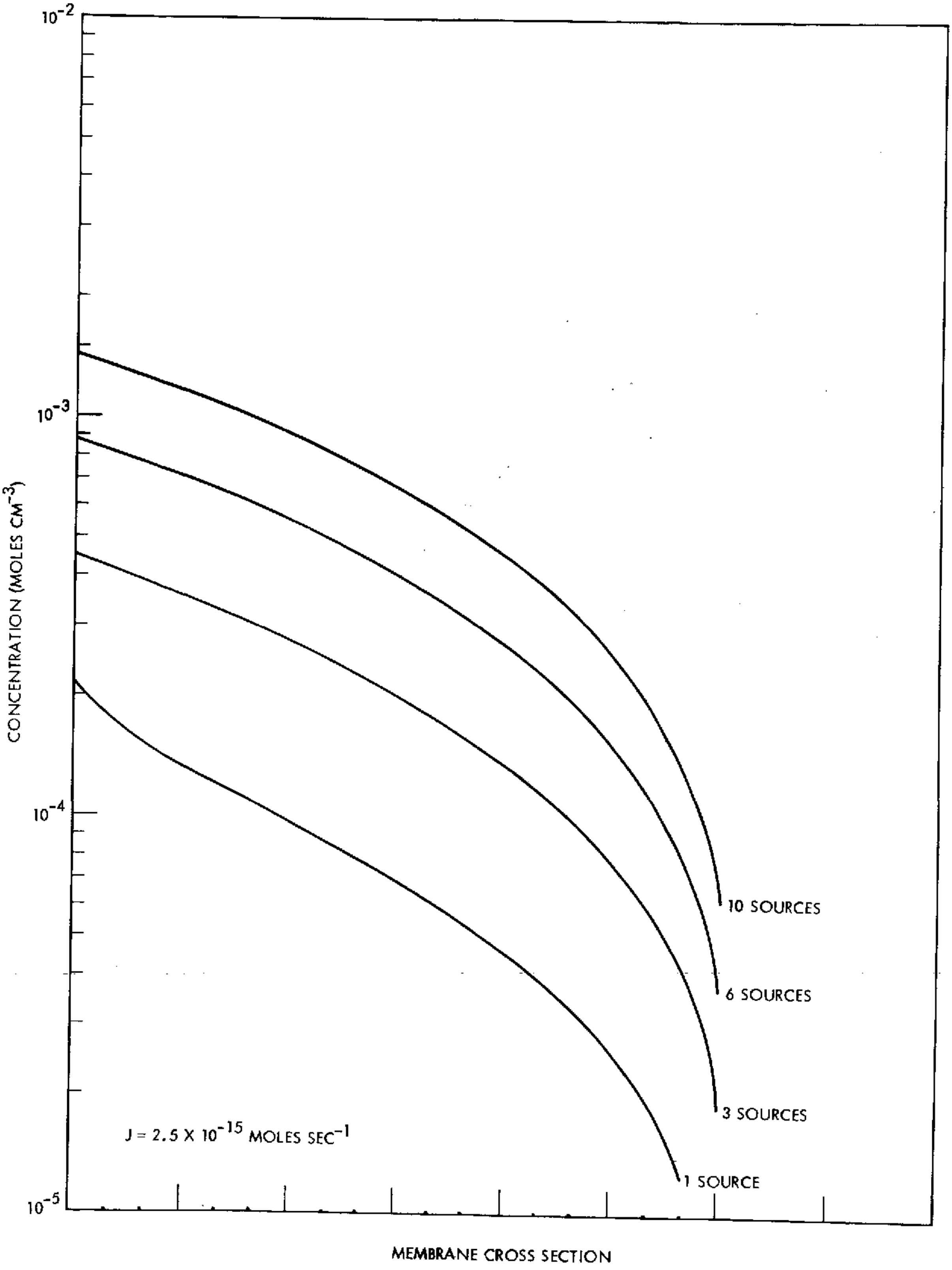

Figure 4. Reduction of Number of Sources - Effect on Steady State Concentrations

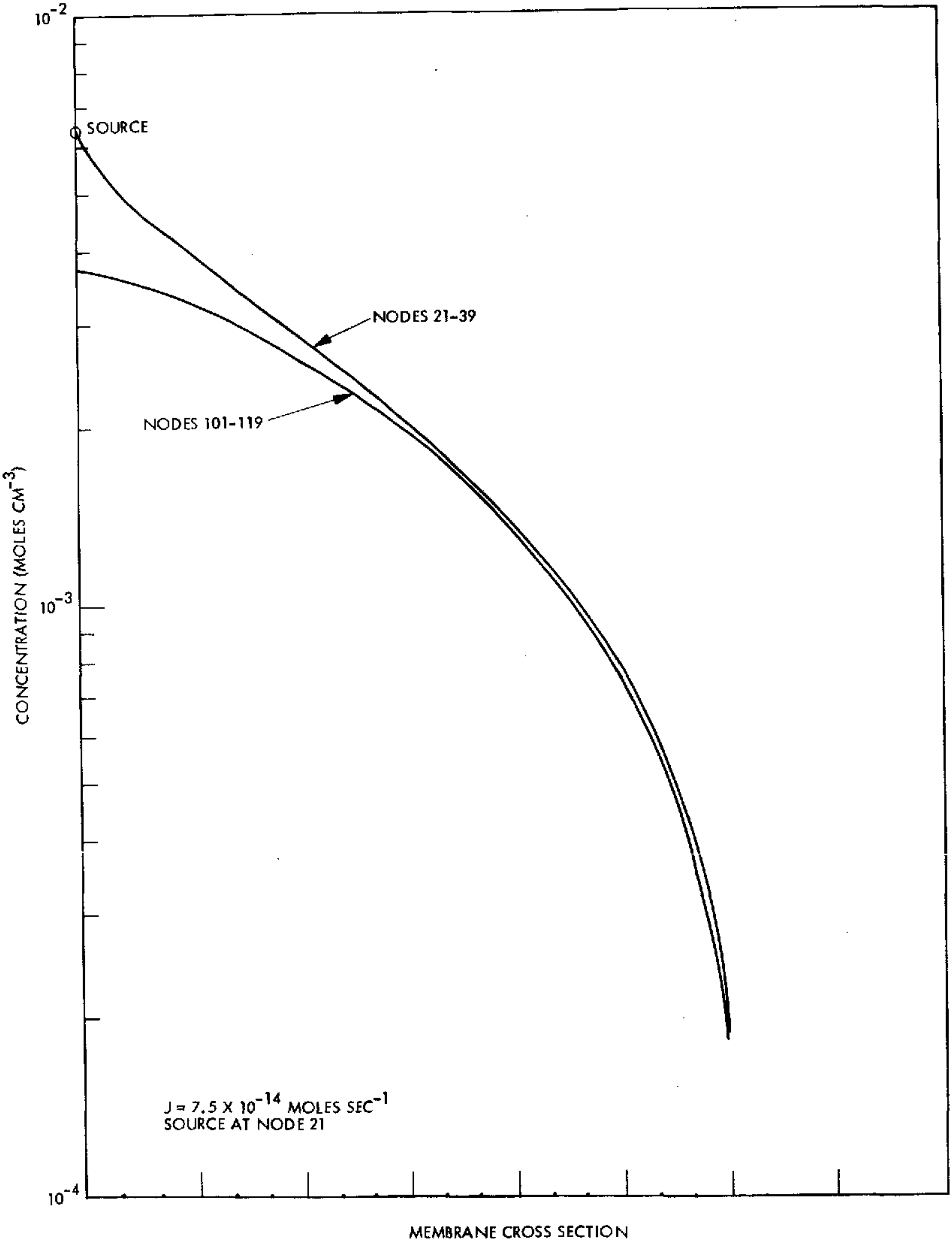

Figure 5. Isolated Source Steady State - Effect of Position

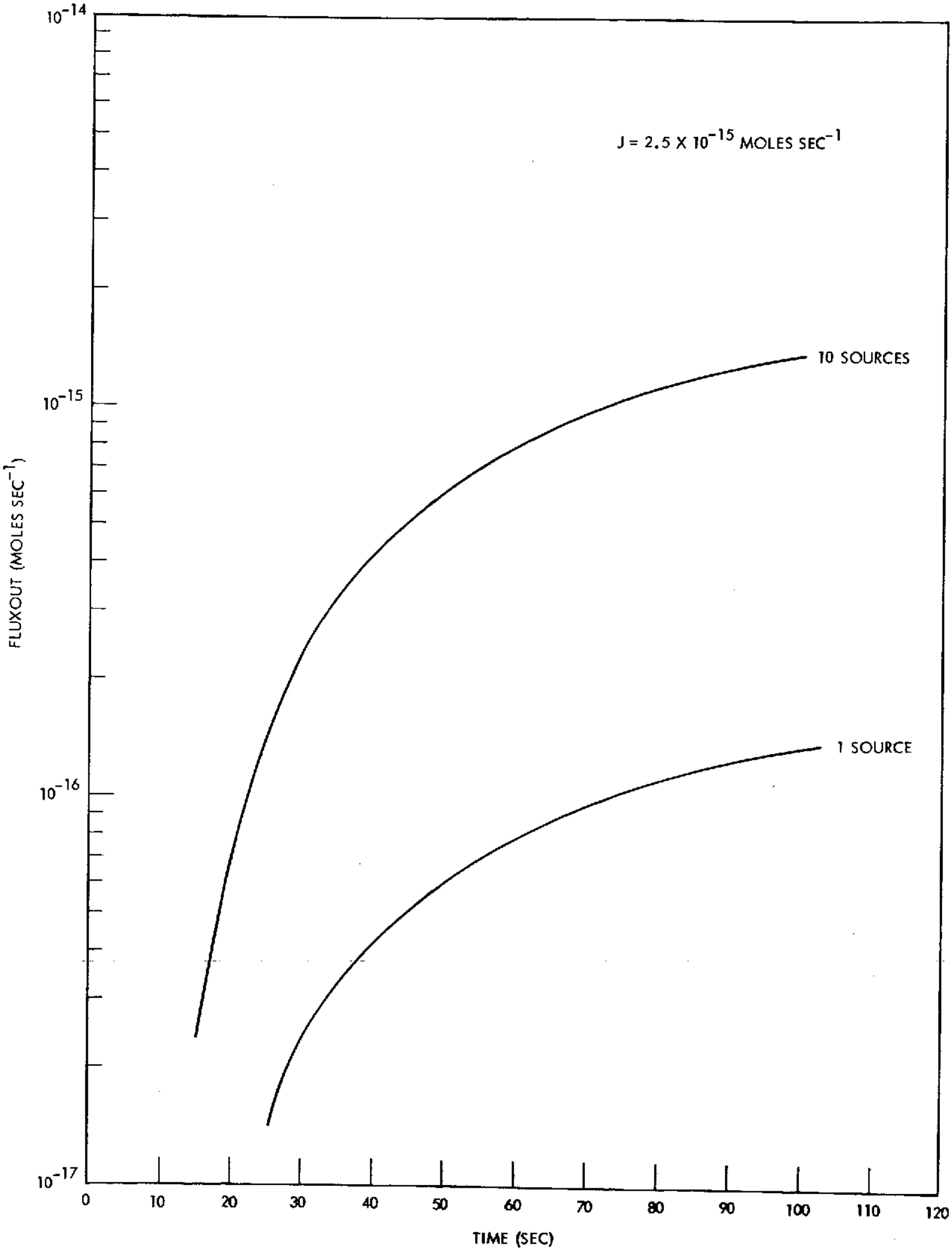

Figure 6. Effect of Reduction Number of Sources

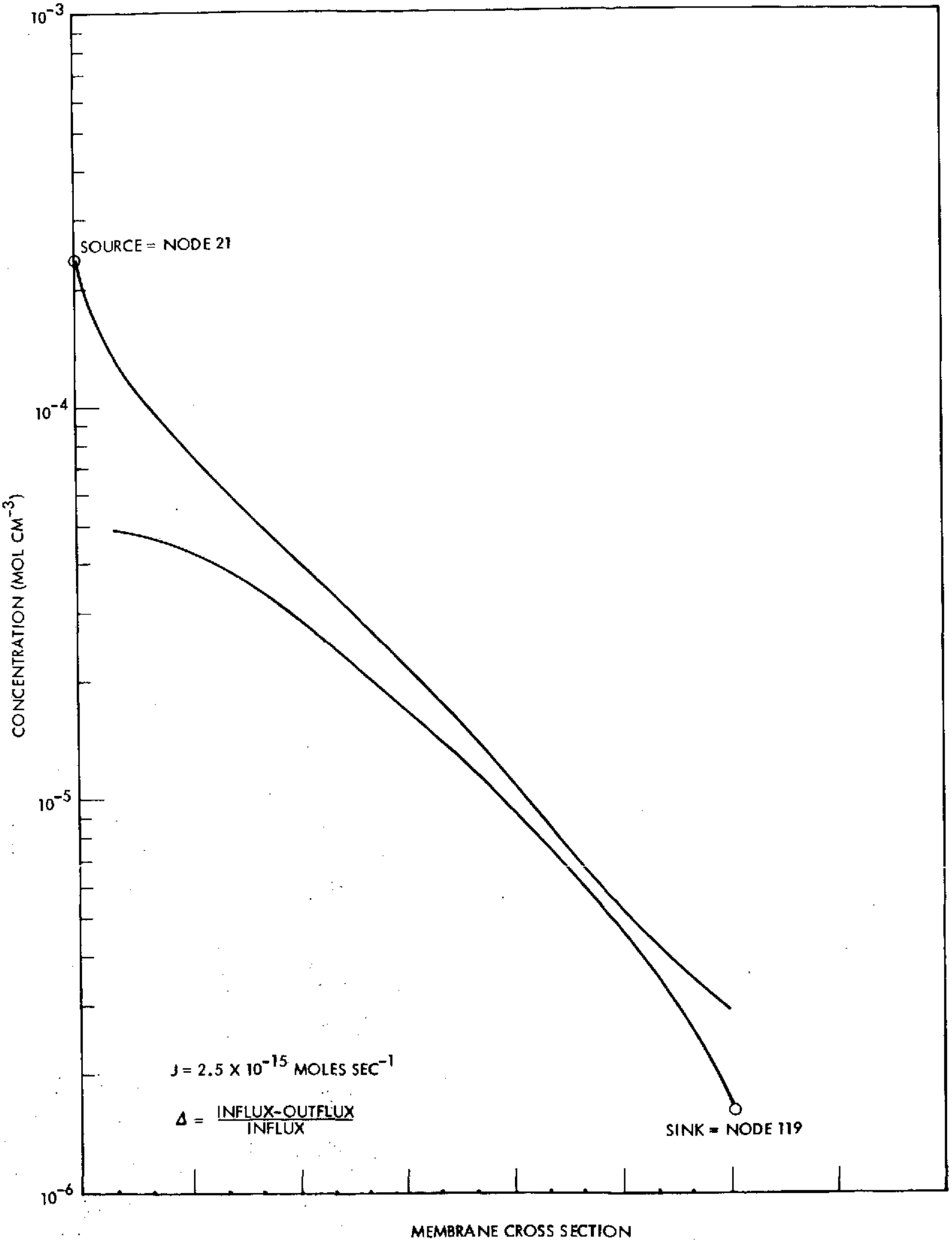

Figure 7. Isolated Source - Isolated Sink Effect of Position - Blocked Surfaces on Concentrations for $\Delta = 0.95$

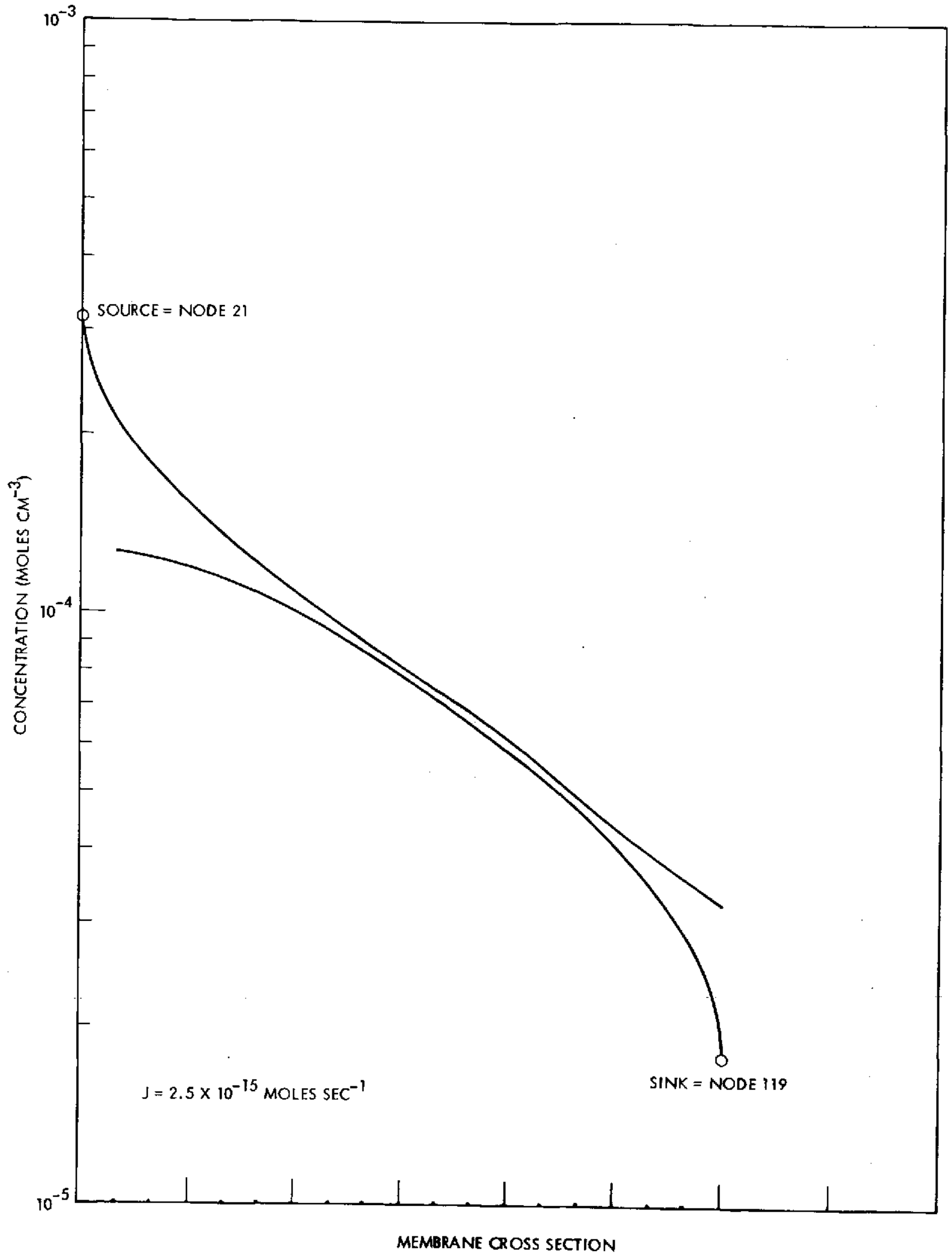

Figure 8. Effect of Isolated Source and Sink, Blocked Surfaces, and Position on Steady State Concentrations

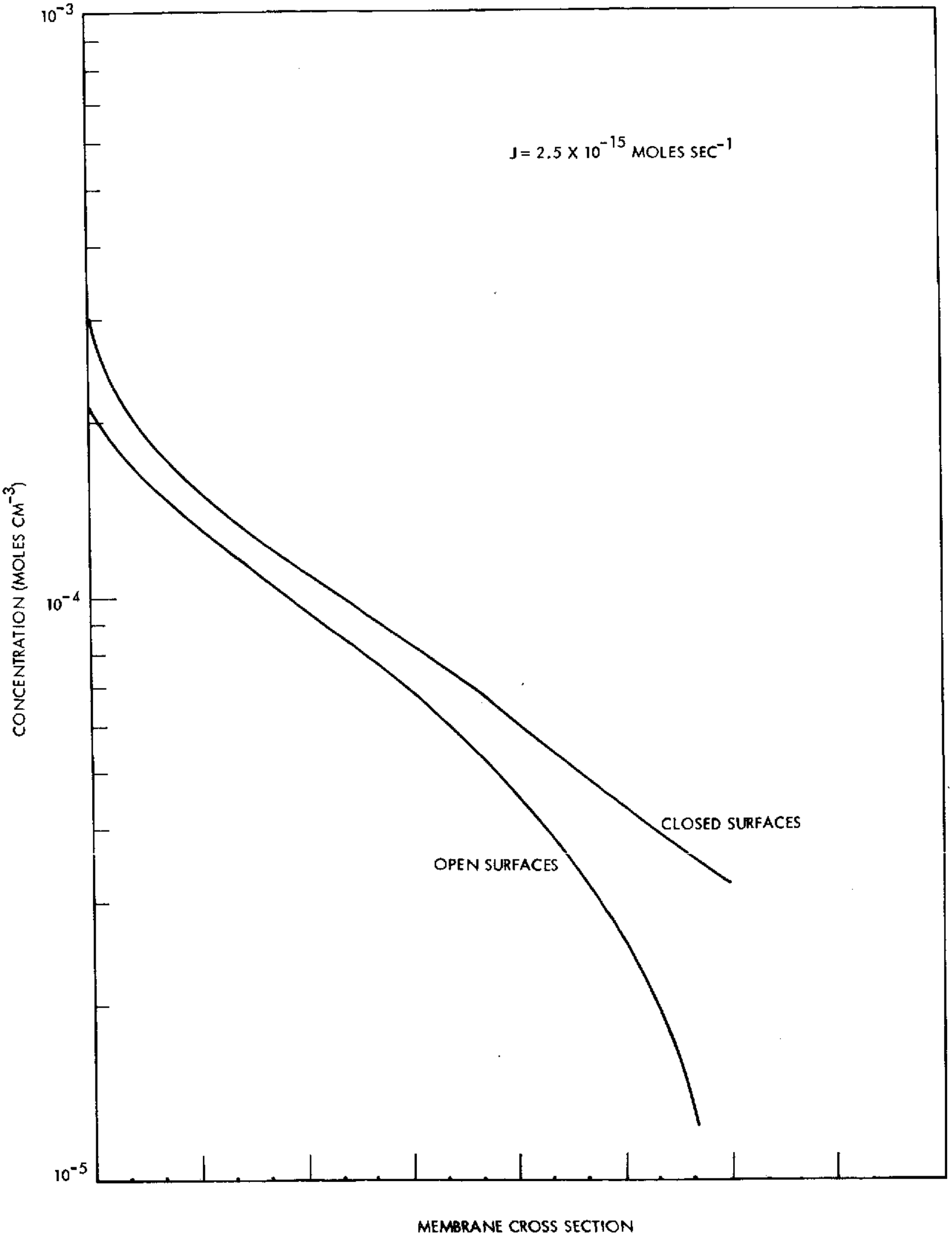

Figure 9. Effect of Blocked Surfaces + Single Source on Steady State Concentrations

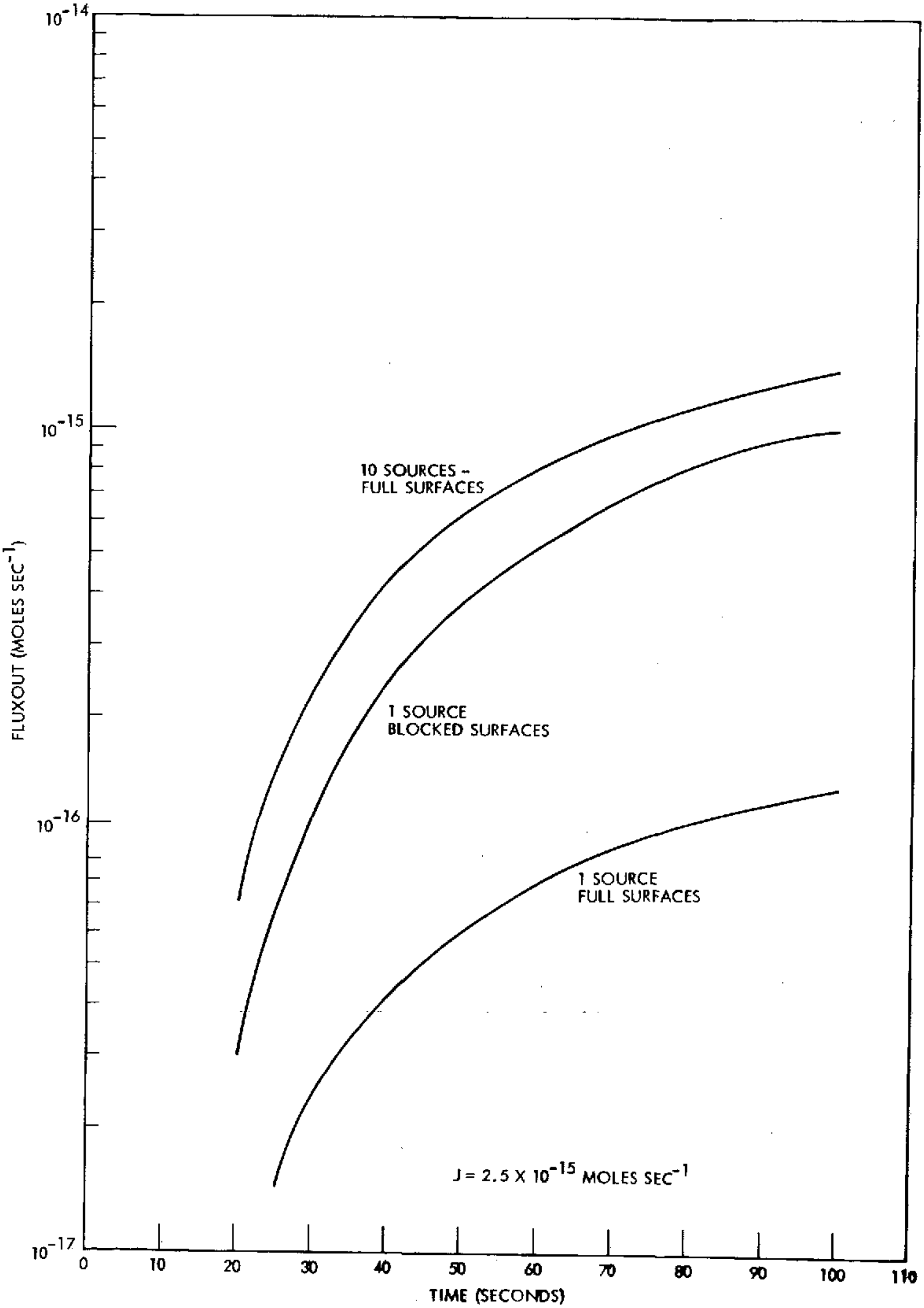

Figure 10. Effects of Surface Blocking

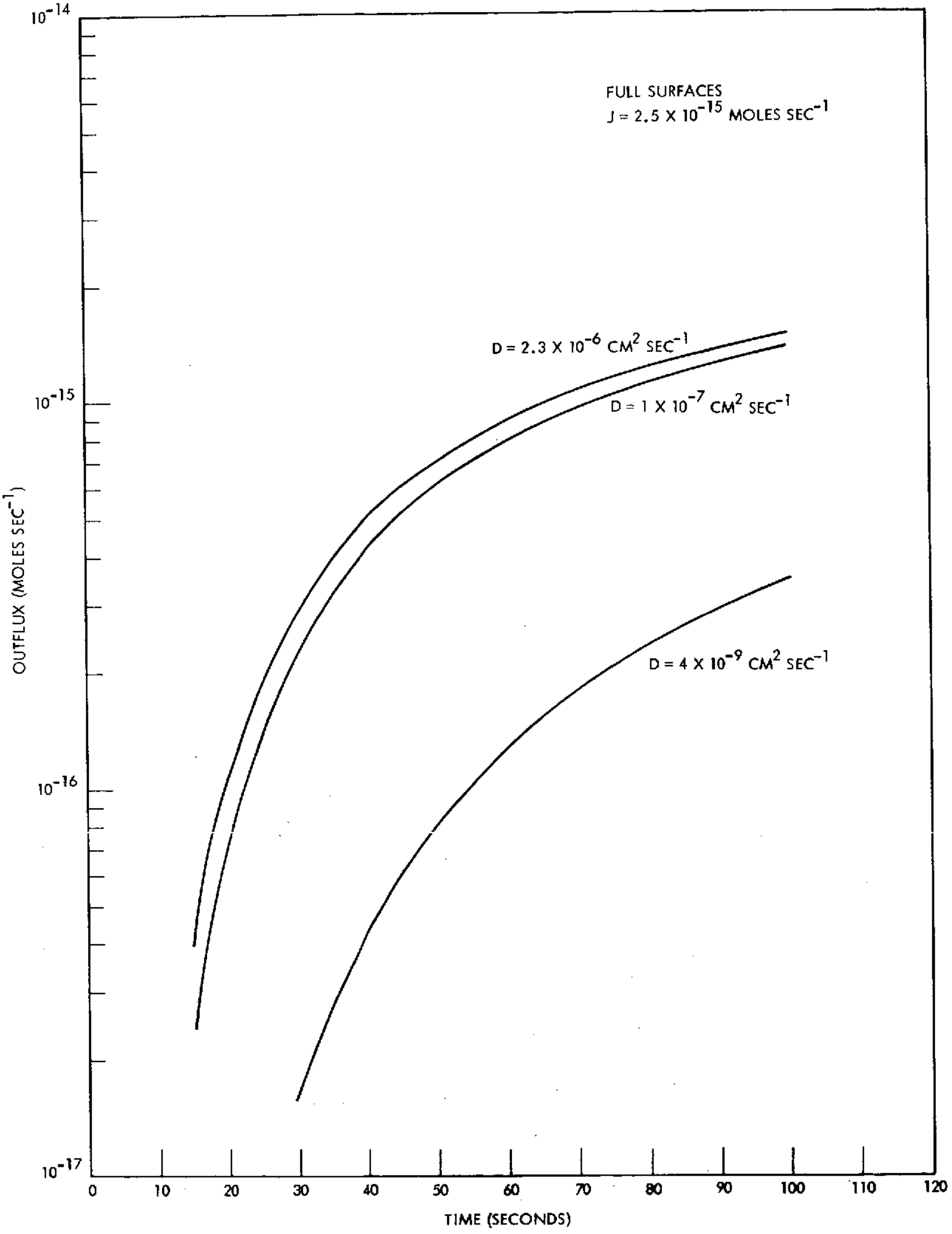

Figure 11. Effect of Surface Diffusion Coefficient

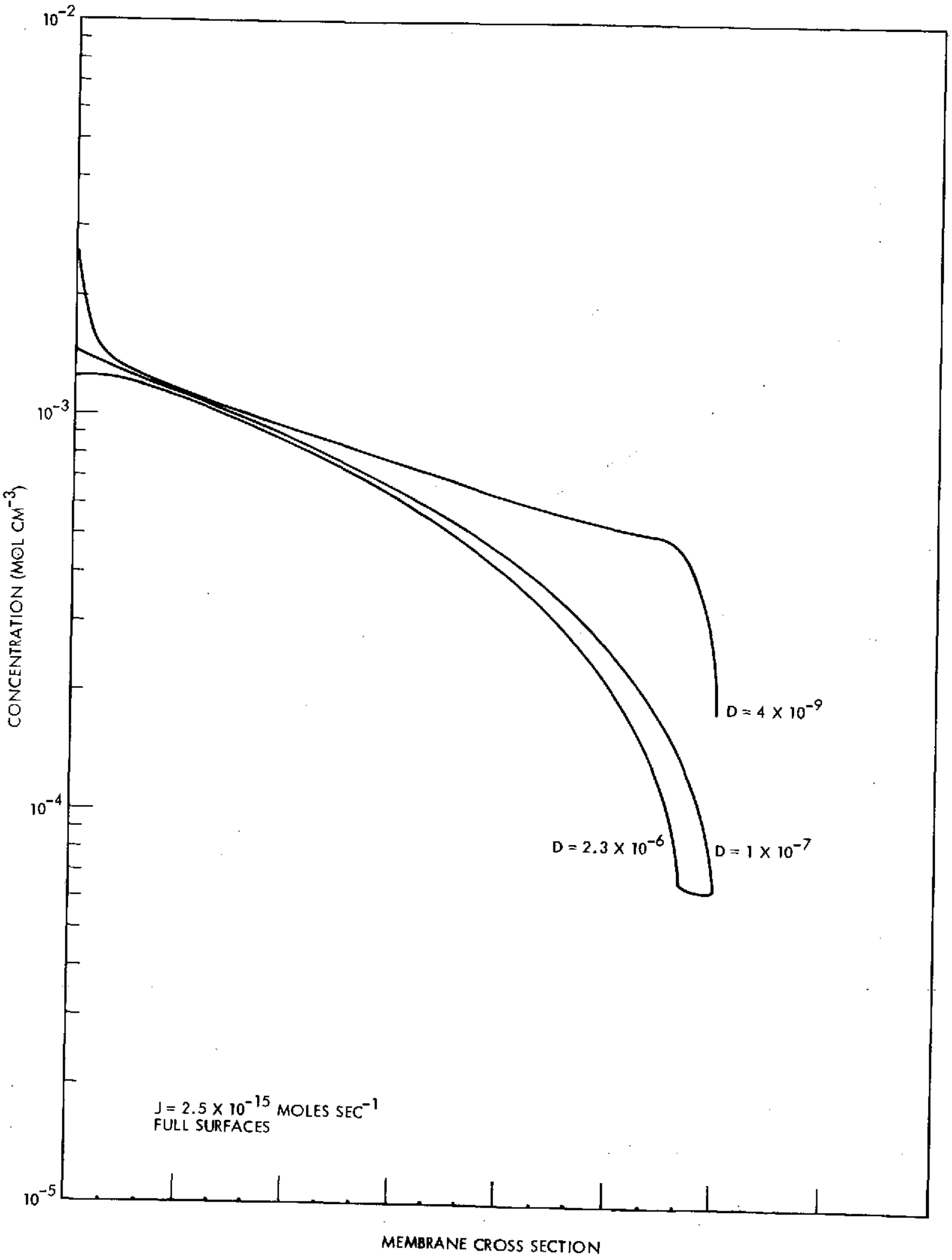

Figure 12. Effect of Surface Diffusion Coefficient on Steady State Concentrations

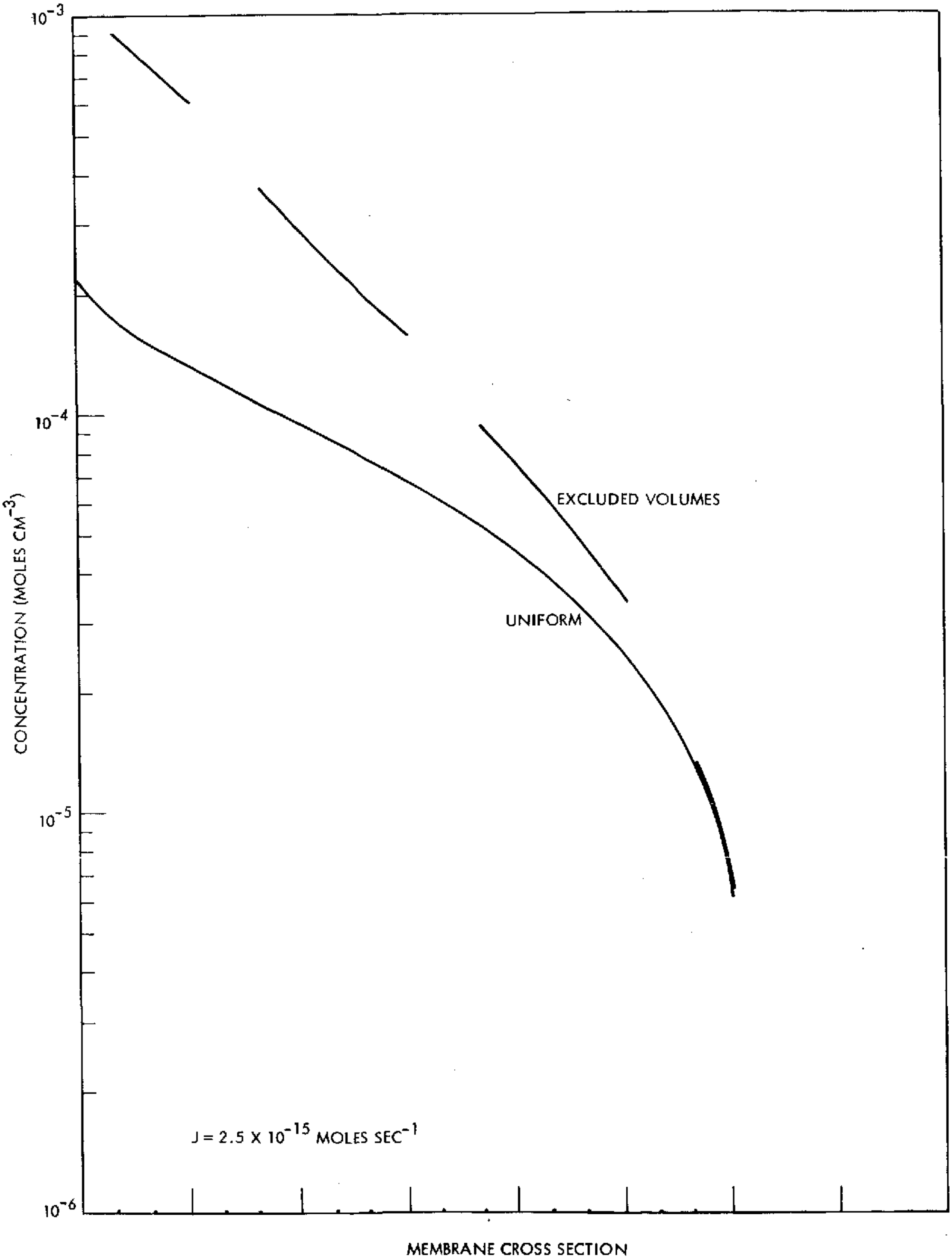

Figure 13. Effect of Excluded Volumes on Steady State Concentrations (Isolated Sources)

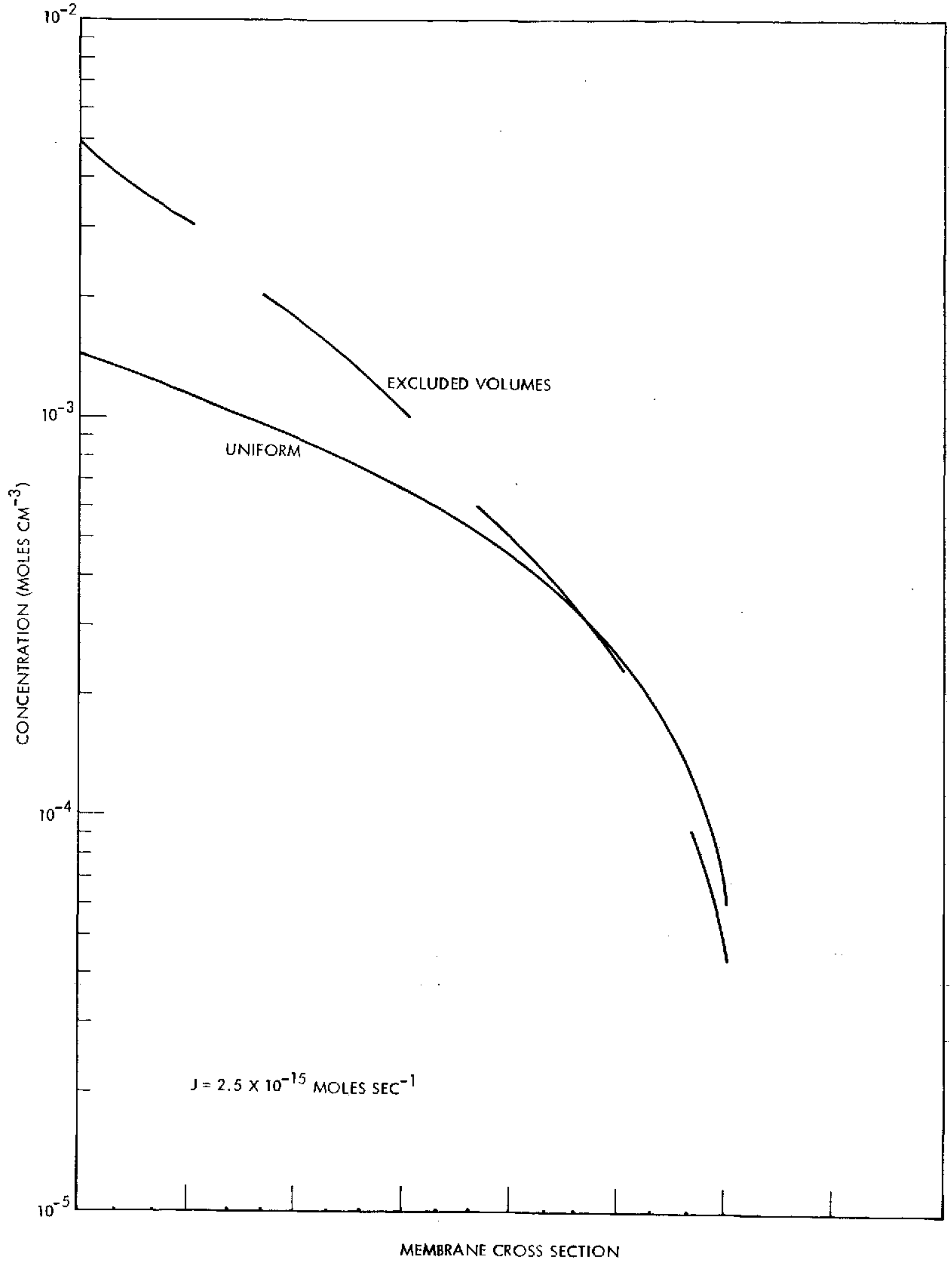

Figure 14. Effect of Excluded Volumes on Steady State Concentrations (Full Surfaces)

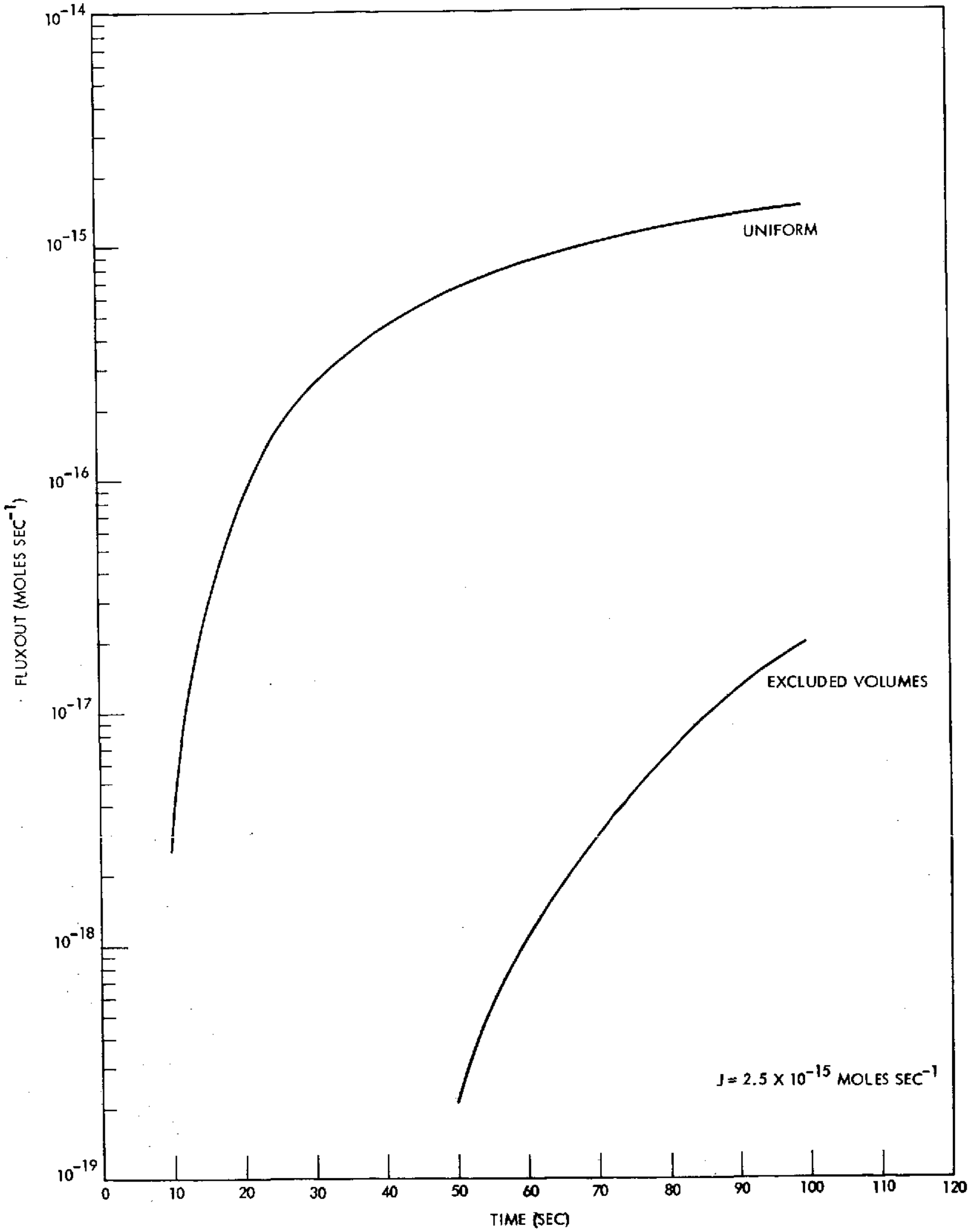

Figure 15. Effect of Excluded Volumes on Fluxout (Full Surfaces)

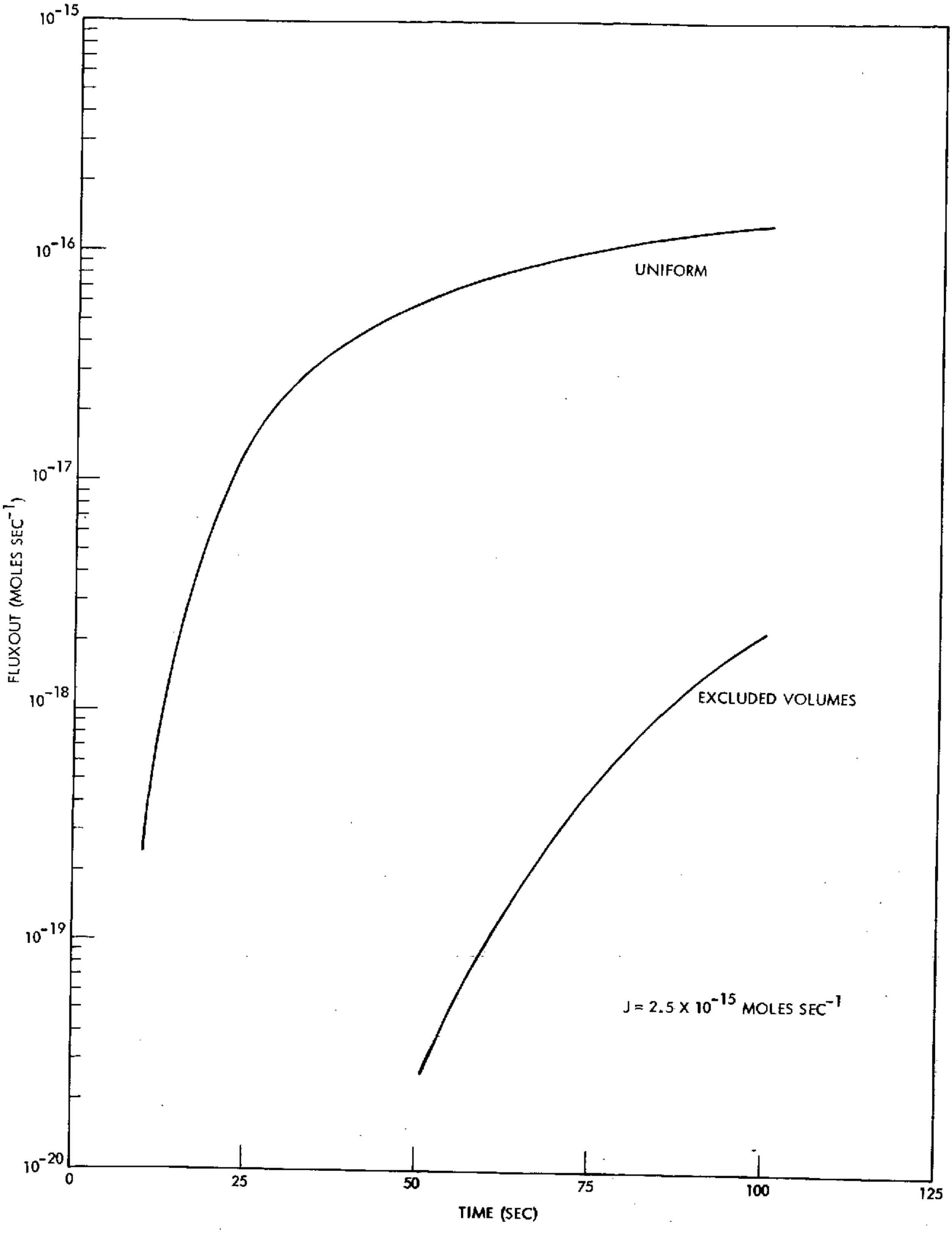

Figure 16. Effect of Excluded Volumes on Fluxout (Isolated Sources)

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