NBSIR 87-3635

The Characterization of Microenvironments and the Degradation of Archival Records: A Research Program

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THE CHARACTERIZATION OF MICROENVIRONMENTS AND THE DEGRADATION OF ARCHIVAL RECORDS: A RESEARCH PROGRAM

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U.S. DEPARTMENT OF COMMERCE, Clarence J. Brown, ***Acting Secretary***
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Director***

EXECUTIVE SUMMARY

E1. INTRODUCTION

The National Archives and Records Administration stores an enormous volume of records, and protecting them from degradation is a matter of great concern. Because the temperature and the condition of the atmosphere in the storage areas are important in controlling the rate of degradation of the stored records, these areas (the "stacks") have temperature and humidity control. However, atmospheric pollutants such as particulate matter, NO_x, SO_2 and ozone cause degradation of records, (see, e.g. reference (1)), and while in some cases the removal of air pollutants from the external air by the NARA air conditioning system is efficient, in other cases it is not (2), with the result that the concentrations of SO_2,and NO_x in the stack atmosphere are above recommended levels (3,4).

However, in the stacks, records (with the exception of books) are stored in containers, and not exposed directly to the ambient environment. The records experience a "microenvironment" which is possibly less aggressive than the macroenvirenment of the stacks. Certainly the use of containers protects the records from particulate matter. If this microenvironment in fact is, or could be made to be, less aggressive, then expensive changes in the air conditioning system might be obviated. For this reason, and because of the intrinsic importance of the topic, a National Academy of Sciences committee convened specifically to study the problem of the preservation of records, made the following recommendation(4):

> NARA should conduct a study of archival containers and microenvironments, including boxes, folders, and polyester encapsulation, with a view to understanding the maximum benefit that can be obtained from particular materials and designs. The committee feels that this is an unexplored area that may yield results highly significant to NARA's preservation efforts.

This report analyzes what is involved in a research program to carry out that recommendation. The main part of the report is concerned with air pollutants; temperature and water vapor are discussed in an Addendum. An analysis the microenvironments experienced by records (principally in containers) is made then the ability to predict useful lifetimes from data on exposure to air pollution is discussed. Finally, there is laid out a suggested research program responsive to the recommendations of the NAS Committee, and which can provide information on the basis of which NARA can make informed judgments about what actions take to further their protection of historical records. This program is described in its entirety in the final section of this summary. It consists of six elements which can be carried out independently. Depending on resources and priorities, some elements of the program can be omitted.

E2. Models and Microenvironments

Unless the container that contains documents is impermeable to matter and heat, the microenvironment experienced by records is not constant, and changes as the macroenvironment of the stacks changes. Material can be exchanged between the microenvironment inside the container and the macroenvironment outside of it by diffusion through the walls of the container or any gaps or openings in them, or, if there are gaps or openings, by pressure or temperature changes. However, the container will slow down and dampen those changes and thus can, at least in principle, provide protection of documents. With complete sealing, or encapsulation, new and serious effects may arise because of the possibility of autocatalytic degradation caused by the degradation of the enclosed documents.

To study these effects, several mathematical models of the actual situation were analyzed to determine the microenvironments and changes in them in various situations. These models were

1) An empty container. This is not a situation that arises in practice, but was analyzed for orientation purposes. As will be seen, the results are quite instructive.

2) A container holding reactive contents.

3) Containers with reactive walls.

4) Books and folders.

5) Sealed, impermeable containers; encapsulation.

6) Recesses.

7) Temperature and Water Vapor. (Discussed in an Addendum.)

Each of these is discussed in a separate section of the report. The approximations, both mathematical and physical that had to be made are discussed in detail there. Because of these approximations, the numerical results obtained have only qualitative or semi-quantitative significance. It is felt, however, that the conclusions drawn from the analysis will be valid. The container used as a prototype in the calculations is shown in Fig. 1. It is style F in the NARA specifications for archival boxes.

The analysis was done for an isolated container, not one stacked on shelves with others. This is the most severe condition. The results are easily translated to stacked containers.

In this summary, only the conclusions of the analysis will be presented, with only enough discussion to place them in context.

E2.1 The Empty Container

This model is the simplest that can be devised. It is useful for orientation purposes and to provide the relative importance of the three mechanisms of transport into and out of the container. As mentioned above, these are diffusion through the walls; diffusion through gaps; and transport through gaps by pressure and temperature changes -- called the "breathing" modes.

If a container with an interior atmosphere at a given concentration is suddenly placed in an external atmosphere that has ten times the concentration of pollutant, the concentration vs. time curves for the interior concentration are given in Fig. 3. If the concentration change is different from the factor of ten used here, the curves are easily scaled. The time scale for the process remains the same. The right hand curves are for diffusion through the walls for two values of the diffusion constant, and for the empty container and one filled with inert documents. The left hand curves are for diffusion through gaps. The important point is that diffusion through gaps, for this particular container is about 1000 times as fast as diffusion through the walls, and that equilibrium with gaps is established in a few hours. Pressure and temperature cycles of the idealized kind shown in Fig. 5, with the pressure changing from 29 in. Hg to 31 in. Hg with a weekly cycle, and the temperature varying from 19C to 20C with a daily cycle, cause equilibration to occur at approximately the same time scale as diffusion through the walls. The curves are given in Fig. 6.

The principal conclusions to be drawn are

1. For gaps or openings of the size in the prototypical container, diffusion through the gaps is much faster than diffusion through walls. Indeed, diffusion through the gaps is so fast that for all practical purposes the container might as well be open. This is a result of the high diffusion coefficient of gases.

2. Pressure and temperature driven transport, for the temperature and pressure excursions considered here, are about as effective as diffusion through the walls as a means of transport.

3. If the exterior concentration cycles (as it does for NO_x in the NARA stacks), for a container without gaps the cycling inside the container is very small. For the container with gaps, the cycling inside the container is about the same as it is outside.

4. The time scale of the changes is given by $V\ell/ADS$, where V is the volume of the container; ℓ the thickness of its walls or gaps; A the area of the walls or gaps; D the diffusion coefficient of the walls or gaps; and S is the solubility of the pollutant in the wall material. Hence the time scale is determined by the dimensions of the container through V, ℓ, and A, and by the material of construction through D and S. Note that the quantity A (and ℓ for gaps), and hence the time scale of the changes, will depend on how the containers are stacked.

E2.2 The Container With Reactive Contents

The model considered here is a container holding contents that can react with the pollutant. Entrance of the pollutant into the container is by diffusion, either through the walls or gaps. The example used is SO_2 in paper. As discussed in Sec. 2.9 of the report, SO_2 first diffuses into paper, then is converted by a metal catalyzed reaction into SO_3 and thence sulfuric acid, which then catalyzes the hydrolysis of paper, leading to degradation. Thus, when a container holds paper documents, SO_2 that enters the container will diffuse into the documents and then react to form SO_3. Approximate values of both the diffusion coefficient and the reaction rate constant are deduced in Sec. 2.9. The interior concentration of SO_2 is thus controlled by both its rate of entry and its rate of reaction. Moreover, knowing the microenvironment, the increase of reacted SO_2 (i.e., SO_3) in the paper can be calculated. This is done in Sec. 2.6. The important assumption that was made was that the contents were loosely packed so that diffusion of SO_2 into them was not the rate determining factor.

The results are shown in Figs. 7-10. The situation analyzed is as follows. At a given time, documents which are at equilibrium with their surroundings are place in a container, which is then closed. Fig. 7, for diffusion through walls shows what happens to the microenvironment for two different values of the reaction rate constant. At first the concentration of SO_2 in the box does not change as the SO_2 in solution in the contents reacts. As this is used up, the concentration in the box decreases, eventually reaching a value determined by a combination of reaction rate and the rate of diffusion into the container. For the slow reaction rate, diffusion maintains a value of the concentration of about 0.6 of the original, but for the more rapid reaction, the concentration drops to the very low value of 0.0044 because diffusion cannot keep up with the reaction rate at any higher concentration.

Fig. 8 is the same except that diffusion is through gaps. Here, in both cases, diffusion can just about keep up with the rate of reaction. The contents might almost as well be in the open.

Figs. 9 and 10 give the concentration of reacted species in the paper as a function of time. Fig. 9, for diffusion through walls, shows that reaction proceeds as the original SO_2 in solution is used up, then levels off, and then proceeds at a lower rate. (Note that this is a doubly logarithmic plot.) For the high reaction rate, considerable protection is provided, but less so for the slow reaction rate. If the box were impermeable, i.e., the diffusion coefficient were zero, complete protection would be provided,but then other problems, discussed under "Impermeable Containers; Encapsulation", would be encountered.

Fig. 10 is the same as Fig. 9, but for diffusion through gaps. The reaction rate is just about what it would be in the open. Essentially no protection is provided.

The significant conclusion drawn from this analysis is that containers can provided protection from the macroenvironment, but provided they have no gaps in them. As is evident *a priori* and is shown by the analysis, reaction cannot proceed more rapidly than material is provided by transport into the box. It follows that if containers are impermeable, complete protection from pollutants is provided, but then other and possibly serious problems arise as will be discussed later under "Sealed Impermeable Containers; Encapsulation".

E2.3 The Container With Reactive walls

Of the various cases investigated, this one appears to hold the most promise for the protection of documents. The reason for this is easy to see. If the container reacts with the pollutant as it diffuses through the walls, then the pollutant may never get into the container. In due course the container may be destroyed, but the contents would have been protected. The container is sacrificed to save the contents, much as is a sacrificial anode in corrosion protection.

This may already be the case with at least some of the NARA containers. Archival boxes of the type chosen as prototypical containers are already specified to contain 3% $CaCO_3$. All experts consulted on this project have remarked that SO_2 an NO_2 would react with the $CaCO_3$ in their passage through the walls, and ozone would probably react with the walls even if there were no $CaCO_3$ present. Moreover, if there are any gaps, but if they are long and narrow, protection could still be provided, for in the passage of a pollutant through the gap, it could diffuse to the container walls and there react with them, preventing its entry into the container.

The important model solved in this problem is a container with reactive walls filled with reactive contents. Unfortunately, mathematical difficulties preclude the solution to this problem to give concentration-time curves like those previously described. The best that could be done within the time and resources available was a solution at steady-state, i.e., after all transients had died out. The results are given in Table 6. In this table, the reaction rate constant of the contents is k_c and that of the walls is k_w. Then, various values of these quantities were investigated. They represent a box made of pure rag paper holding pure rag contents at the one extreme, and a box made of newsprint holding newsprint contents at the other. The important result is in the final column of this table. This column gives the rate of reaction of the contents compared what it would be in the absence of a container. The results depend on the diffusion coefficient, but except for the case of a pure rag box holding pure rag contents (not a very likely situation, and one probably not requiring much attention in any case), essentially complete protection is provided. Again, however, the autocatalytic degradation problem needs to be considered, and will be in the section "Impermeable Containers; Encapsulation".

E2.4 Books and Folders

This analysis was directed at the mechanism by which a pollutant attacks book pages. Simply stated, the problem is, "Does the pollutant diffuse in through the edge of the book sheets or does if diffuse in between the sheets and then spread laterally?" It will be clear that the looser the sheets are packed, whether in a book or in a folder, the more likely is diffusion to occur between the sheets, because the diffusion constant in gases is much higher than in solids.

This problem was addressed by applying the concept of grain boundary diffusion used in metallurgy and is discussed in Se. 2.8. To do this, it is necessary to know the thickness of the intersheet region and its diffusion constant. This would also be necessary in any other method of analysis. This thickness obviously depends on how much pressure is applied to the book or to how tightly documents are packed in folders. But simply to get some bounds on the time scales involved, crude measurements were made on the thickness of books as compared to the sum of the thickness of the sheets. It was found that the thickness of the books was roughly 10% greater than the total thickness of the sheets, so that the intersheet region has a thickness of about 10% of the sheet thickness. Then as an upper limit for the diffusion constant, a value for diffusion in the gas phase was chosen

The results are totally contrary to experience. They show that if the diffusion constant were that in the gas phase, after one day or so the whole book would be permeated by pollutant. The brown discoloration commonly observed around the edges of book pages, would instead, to the extent it is associated with pollutants, be uniform over the sheet. To the extent that these very crude results have any meaning, they indicate that the diffusion constant between sheets is more likely to be nearer to that in the solid than in the gas phase. The whole book acts almost like a solid block of paper. The inter-sheet region is very likely a quite complicated thing, perhaps corresponding to diffusion through a percolation maze.

On the other hand, the results do indicate that if sheets are loosely packed, then the high diffusion constant in the gas phase assures that they quickly become permeated with pollutant.

E2.5 Sealed, Impermeable Containers; Encapsulation

As has been seen from the analysis of various models, and is obvious *a priori*, if record documents are placed in sealed containers impervious to pollutant, then they are protected from the pollutant. The question then naturally arises, "Why not store records on sealed, impermeable containers?"

Experience has shown that unless the paper stored is of high quality and resistant to degradation (like the pure alpha-cellulose paper in the Constitution and Declaration of Independence cases, or photographic print paper), sealing or encapsulation is harmful. Moreover, sealing good paper with poor paper may be harmful for the good paper. The reason for this is the degradation products of the poor paper. These products appear to be acidic and hence catalyze degradation by hydrolysis, leading to an autocatalytic situation. The contents of a sealed, impermeable container "stew in their own juices", so to speak.

While this is the opinion of all the experts consulted in this project, laboratory data on this effect are scanty. Only two experiments comparing the rate of degradation in a sealed capsule with that in the open but otherwise identical conditions are known to us (27,28). In one of these (27), degradation was carried out at elevated temperatures in a sealed glass ampoule and compared to degradation in the open, but otherwise the same conditions. Degradation was more rapid in the ampoule, but this is not a definitive test because the pressure (particularly of oxygen) was higher in the ampoule than in the open. In the other experiment (28), degradation in polyester envelopes was compared to degradation in the open. It was found that degradation was more rapid in the envelope. However, it was found that the acceleration of degradation inside the envelope could be eliminated by including in the envelope paper with an alkaline reserve. This indicates that whatever the degradation accelerating substances are, they are probably acidic, and may be transmitted via the gas phase.

The identification of these substances, and of methods of inhibiting them are considered to be projects of high priority.

E2.6 Recesses

There are numerous regions or spaces, e.g., an empty shelf, or the region over the tops of books packed on shelves, that have limited access to the ambient stack environment. These spaces, which are referred to as "recesses", provide for the possibility of a microenvironment, and an analysis was carried out to see how much this microenvironment differed from the macroenvironment of the stacks.

In many, and perhaps most, cases, these recesses can be considered to be a rectangular parallelipiped open on one side to the ambient stack atmosphere, and with the other five sides consisting of impermeable material. It is clear that the slowest mode by which this recess can exchange pollutant with the ambient stack atmosphere is by diffusion; any convection that takes place will only hasten the exchange. Hence a diffusion investigation was made of this recess.

This is a standard problem in diffusion. It is readily shown that,under quite unrestritive conditions, the rate at which pollutant spreads into the recess is independent of the lateral dimensions of the recess. It was then calculated that for a recess one meter deep, after 12 hours the environment at the bottom of the recess is essentially the same as the ambient environment. Any convection that may take place will shorten the time needed to arrive at equilibrium.

E2.7 Temperature and Water Vapor

These microenvironments are treated in an Addendum. Temperature is important because it influences the rate of chemical reactions, specifically degradation reactions in this context. Temperature distributions following a sudden change in temperature were calculated for the case of an isolated book; a container tightly packed with documents; and a shelf of books. Results for the temperature distribution as a function of position and time are given in Figs. A-1 to A-3. From these, knowing the rate law for a given reaction, the extent of reaction as a function of position can be calculated. The important result was derived that in a macroenvironment in which the temperature varies, the extent of reaction at the surface of any one of these items will be greater than in the interior.

The analysis for water vapor largely follows that for pollutants. The methods are the same, but the data are even more scanty,and somewhat more drastic approximations had to be made. The well-known high solubility of water vapor in cellulose dramatically lowers the rate at which a box filled with paper documents comes into equilibrium with the external environment as compared to an empty box. In effect, the documents enormously increase the volume of the box. Also, water participates in hydrolysis, but there is so much water in paper that very little is used up during the hydrolysis. For this reason, and because the initial conditions upon storage are not usually known, impermeable containers are not practical for controlling moisture content.

E2.8 Conclusions

There are several conclusions that can be drawn from the analysis and that are very likely independent of the assumptions made in it.

1) The microenvironment inside a container communicates with the macroenvironment outside it by diffusion through the walls of the container; by diffusion through any gaps or openings in those walls; or by pressure or temperature changes if there are gaps in the walls.

2) For an empty container with inert walls, the interior microenvironment eventually becomes the same as the macroenvironment if the latter is constant, or its average if it is fluctuating. If there are any gaps in the walls, the interior environment is always very nearly the same as the exterior environment, and follows any changes in the latter with only a small time delay. The time constant, or "relaxation time", for any changes in the microenvironment in the absence of gaps in the walls is given by $V\ell/ADS$, and hence depends on the design of the container through V, A, and ℓ, and on the materials of construction through D and S. If there are any gaps, the expression for the relaxation time is the same but without S, and its value is very small compared to diffusion through the walls.

3) Pressure and temperature cycles, for the ranges of change and time scales assumed for those changes, are about as effective as diffusion through walls in providing communication between the inside and outside of containers.

4) If the container holds reactive contents, i.e., the contents react with the pollutant(s) in question, then, in the absence of gaps in the walls, the microenvironment inside the container can be substantially different and more benign than the macroenvironment outside it. If gaps are present, then the microenvironment can be essentially the same as the macroenvironment.

5) If the container walls can react with the pollutant(s) in its (their) passage through them, then essentially complete protection from the pollutant can be provided. This may even hold if there are gaps in the walls, provided the gaps are long and narrow.

6) The diffusion constant for the interface between sheets in a book is probably much lower than for diffusion in a gas, and may approach the diffusion constant in the solid phase.

7) Sealed, impermeable containers will obviously prevent any communication between the inside and outside of the container and hence provide complete protection from the exterior pollutants. However, if the contents are reactive, they may give off degradation products that

catalyze further degradation. (The contents "stew in their own juices"). The option of sealed, impermeable containers is limited to such items as very high quality paper, safety film, and perhaps magnetic recording tapes.

8) Unless recesses are very deep, the microenvironment in them is essentially the same as the macroenvironment.

9) There is a very limited availability of data in the literature with which to make calculations from the models and to check them.

10) Because of the Arrhenius dependence of rate constants on temperature, in a fluctuating temperature environment the extent of reaction in the surface regions of books and document boxes will be greater than in the central regions of the items.

11) The high solubility of water vapor in cellulose dramatically lowers the rate at which the interior of a box filled with paper documents comes into equilibrium with the external environment as compared to an empty box.

E3. Degradation and Its Prediction; Data Availibility

This section is concerned with the prediction of permanence-- the so-called study of accelarated aging. The primary focus is on degradation caused by air pollutants, and the principal interest is paper. Unlike the previous section of the report, no analytical work is done; the discussion is primarily a review of the literature. First there is a general review of paper degradation; then a review of degradation by air pollutants; then a general discussion of accelerated aging and a specific one on air pollutants; then finally a literature survey of transport coefficients and reaction rate constants for pollutants in various polymers.

The course of degradation is broken down into three steps. First, and most basic, there are chemical reactions, e.g., hydrolysis of cellulose. These lead to what are termed "chemical measures" of degradation, e.g., the decrease in degree of polymerization. These in turn lead to "physical measures" of degradation, i.e., those properties of paper that affect its performance in service, e.g., fold endurance. Now, a pollutant reacts with paper leading to a chemical change (a chemical measure of degradation) which may lead to a physical change (a "physical measure") that makes the paper no longer useful. In the ideal world, the relationship between these three: basic reaction, chemical measure, and physical measure, would be known, and accelerated aging tests could be devised on a logical, scientific basis. But even in the absence of this knowledge, this ordering provides a logical skeleton for the analysis, and is the point of view adopted in the discussion.

The summary of the review is best expressed by the conclusions, which are as follows

1. Degradation can be characterized by a number of chemical and physical measurements. The chemical measures are closer to the basic chemical

reactions that occur on degradation, but the physical measures are more closely related to the actual utility of record documents.

2. The relationship of the physical measures of degradation to the basic chemical reactions that occur in degradation are known in only a qualitative way. To put accelerated aging on a firm basis, this relationship should be determined insofar as possible. This is likely to be a long and continuing task.

3. The degradation products of paper and other record materials are known or suspected to increase the rate of degradation, and hence to cause degradation to be autocatalytic. What these degradation products are is not known. It is suspected that in the case of paper they are acidic and promote further degradation by hydrolysis. It is not known if they are gaseous and hence capable of transmission through the gas phase.

4. Sulfur dioxide in paper acts by conversion to SO_3, and thence to sulfuric acid. The rate of this reaction is increased by heavy metal ions. This increased acidity causes an increase in the rate of hydrolysis and hence degradation of the paper. Its action on other record or container wall construction materials is not known. It may be inert in some of them.

5. The reactions of NO_2 with cellulose are rather well known, but their relationship to the physical measures of degradation in paper are not. Data on transport properties are not known to us.

6. The action of ozone on records has not been studied. It is known to degrade cotton fabrics under certain circumstances, and to react with cellulose, but its effect on the physical measures of degradation is not well known.

7. The accelerated aging of paper without consideration of the action of pollutants has been a study of long duration, and has resulted in two useful standards. Two important questions remain: the effect of humidity, and the effect of degradation products, which are clearly of central importance if degradation in sealed containers is to be predicted.

8. There are only a few experiments directed at the accelerated aging of paper in the presence of pollutants, and none on other materials of interest as either record or container wall materials. As a simple example of the type of experiment that has not been done, consider the following. The rate of reaction of a pollutant can be increased by raising the concentration or by raising the temperature. However, raising the temperature decreases the solubility, which decreases the rate of reaction. Thus, by simply changing the temperature or concentration alone, their relative effects will not be sorted out.

9. The availability of data on transport properties and reaction rate constants is such that these will have to be determined on the actual materials under investigation when experimental investigations are carried out.

E4. A RESEARCH PROGRAM

E4.1 Introduction

It is clear from the structure of this report, and is evident ab initio, that the problems of concern in this whole question of microenvironments fall into two areas:

1. What are the microenvironments experienced by record documents?, and
2. Given an environment, micro or macro, how rapidly do documents degrade?

The aspects of the environment that are of concern are temperature, relative humidity, pollutant concentration, and the important question of the presence, nature, and action of degradation products. The principal emphasis here is on pollutants and degradation products. Logically, then, the research should address these two areas. This follows the structure of the report, and since conclusions were given at the end of the two main sections of the report, it is necessary to develop a research program that answers the questions posed in those summaries. Here we describe such a program.

E4.2 Microenvironments

In this section of the report a number on models that relate the microenvironment inside a container to the macroenvironment (and any changes in it) outside it were developed. If (a significant "if") these models were known to be correct, then a knowledge of the container dimensions, and the relevant parameters D, S, and k for the various pollutant/container wall combinations would permit the calculation of the microenvironment inside the container. But, as detailed in Sec. 2, a number of approximations had to be made in the development of the models, so their validity has to be checked. Hence an experimental program, supported by theoretical analysis, to check out the models should be considered. While this program might be called, "validation of the models", it should be noted that a great deal of important information on microenvironments will be developed, whatever its intent. Specifically the following experimental investigations are suggested. This largely follows the analysis in the previous text.

E4.2.1 The Container with Inert Walls

This is the simplest of the investigations. While it is probably not applicable to the paperboard container used as a prototype in the report for illustrative purposes, since its walls are probably reactive, it is likely applicable in other cases where the wall materials are inert. This, in turn, is likely to occur only with SO_2, since, as was seen, NO_2 and O_3 are quite reactive. The objective of the investigation is to determine, in this simplest case, how the microenvironment inside the container is affected by changes in the exterior macroenvironment. As far as is experimentally possible, actual containers should be used. The effect of gaps should be studied, for, as was seen in the development, they are likely to be very important, and the "breathing" as well as the diffusion modes should be investigated. Experiments with the container empty and filled with reactive documents should be carried out.

As part of this investigation the coefficients D,S and k will have to be determined for the actual pollutants, wall materials and record materials involved, for otherwise a purely empirical investigation with hardly any opportunity for significant analysis will result. The important point to note is that if the models are verified, or an applicable model is developed, then it is only necessary to measure these coefficients to predict what would occur in a new and untested situation.

It is possible to do at least a part of this investigation (e.g., the empty container) without using a pollutant gas. This is strongly discouraged. Even though it would then be possible to predict what would happen with a pollutant, assuming an applicable model is developed, it would probably not be wise to proceed without actual experiments with pollutants. Moreover, it is unnecessary to use non-pollutant materials. Sulfur dioxide with a convenient radioactive isotope for analytical purposes would appear to be a natural candidate as a pollutant gas.

E4.2.2 The Container with Reactive Walls.

This is viewed as perhaps the most important investigation that can be carried out. As noted in Sec. 2.7, if the pollutant cannot be get through the container walls, then the contents are obviously protected from them. The only question that then arises is the effect of degradation products.

An experimental program that investigates this question could go as follows. First, determine the diffusion and solubility coefficients, and the reaction rate constant for one of the wall material/pollutant combinations. In this case, paperboard with and without $CaCO_3$, and with and without lignin, would seem to be very appropriate, as would SO_2 because of the ease of measurement and because some measurements already exist in the literature (13-15). Then experiments with an actual container to determine the interior microenvironment as a function of the exterior macroenvironment could be carried out. In this case the prototype container, or a similar one, would appear to be highly appropriate. Experiments with and without contents should be carried out. The effect of gaps should be investigated, especially the effect of their aspect ratio, for as pointed out in the text, long narrow gaps might prevent the entrance of pollutants if the wall material is sufficiently reactive.

A full analysis of the experimental results derived from these investigations would very likely require a full solution of the time dependent diffusion problem. (Recall that only the steady state case was used in this report.) This solution was sketched out in Appendix A-9. To apply it would require more theoretical work. This would be desirable but not completely essential. A great deal of progress could be made experimentally with good experimental design and analysis.

This is deemed to be possibly one of the most rewarding of the investigations that could be carried out.

E4.2.3 Degradation Products; Encapsulation

It follows from the discussion in Sec. 2.11 and Sec. 3.4 that if degradation products are not given off, or they do not catalyze further degradation, sealing documents in impermeable containers protects them from an aggressive environment. If degradation products are given off and do promote further degradation, then sealing documents in an impermeable container will still protect them from exterior pollutants but might compound the degradation problem by promoting degradation by the degradation products because these are now prevented from diffusing away from the documents. However, if these products can be removed from the container by the wall material, either by reaction with them , or because the products can diffuse through the walls, the container will at least not worsen the situation. Note that neither of these two kinds of container can prevent the degradation of inherently degradable materials; the best they can do is not to aggravate the situation. There is no substitute for high quality record materials. The first case, in which the products can react with the container walls, might apply to the $CaCO_3$ filled paperboard container, while the second might apply to a polyethylene shrink-wrapped book, although in this case the shrink-wrap might not protect the book from exterior pollutants. This latter situation is in fact a special case of the situation in Sec. E4.2.1, except that here we are now concerned with diffusion <u>out</u> of degradation products, and diffusion <u>in</u> of pollutants.

It is the opinion here that not much can be done on this problem until the degradation products are identified. Are they organic acids, aldehydes, ketones, nitrogen oxides, or what? Are they gaseous or not, and even if not, do they exist in the vapor phase? How are they transferred from one document to another? By diffusion on contact or by transfer via the gas phase?

It is felt that until these questions are answered, only empirical progress can be made While this could prove useful (see Ref. 28), it is felt that modern analytical techniques like gas chromatography-mass spectrometry provide an opportunity for the identification of these products. An experimental progeam on their identification would appear to be very much in order and would begin to answer the vexing questions about the nature and likely effect of these products.

When considering an experimental program, it should be remembered that the primary, and perhaps sole, interest here is on degradation products in the gas phase, for only then is the microenvironment changed. Then the effect of containers becomes relevant. It is interesting and important to know, for example, that the C-6 carbon on cellulose is oxidized to a carboxyl on degradation, but not relevant to the problem of microenvironments. Only if that carboxyl is subsequently released as, say, formic acid, does it affect the microenvironment in the container and hence influence another piece of paper remote from the one in which it originated. An experimental program of this type should include paper of various types as well as leather, pyroxylin containing book bindings, and other materials of interest. An obvious follow-up study is the reaction of these products with wall materials and their diffusion through them.

E4.2.4 The Book Problem; Folders

The problem of the mechanism of entry of pollutants into book sheets was discussed in Sec. 2.8. There, on the basis of a simple calculation, it was concluded that the interface between sheets in a book is probably of a complex nature with a diffusion constant that is probably much lower than for gases, but whose magnitude is hard to estimate. Aside from a more thorough theoretical investigation, no particular course of action suggests itself. Moreover, it is not clear that an investigation of this problem would be very useful. It seems quite clear that the more tightly books and documents in folders are packed, the more the center portions of the sheets would be protected. Their edges, in the absence of a container, will always be exposed to the macroenvironment, however tightly packed, and in a container, the problem becomes one of those already discussed. As a result, no particular research program is suggested.

E4.3 Degradation; Lifetime Prediction

E4.3.1 Introduction

The studies described in the previous section can be relatively short-term, since they have the well defined goal of validating and/or developing microenvironment models, or, as in Sec. 4.2.3, of identifying degradation products. When it comes to the problems of concern in this section, the research tends to be longer range, with goals that, while capable of definition, are not as easily capable of attainment. The problems can be grouped into three categories: the relation of basic chemical degradation reactions to physical measures of degradation; the chemical effect of pollutants on record materials; and accelerated aging by pollutants. We will take up each of these in turn.

E4.3.2 Relation of Basic Reactions to Physical Measures of Degradation

As discussed in Sec 3.2, this is an important area of research since a knowledge of these relationships is necessary to put accelerated on a sound fundamental quantitative basis. A research program in this area would include the identification of the basic reactions involved, and the measurement of their rates and activation energies. While difficult, this is the easy part. The difficult part is relating these to the physical measures. While, for example, a great of work has been done on the relationship between tensile strength and degree of polymerization in cellulose (73), a chemical measure of degradation which can be in turn related to hydrolysis, very little has been done on the relationship for the more commonly used measure of fold endurance. This whole area merits attention, but it should be considered a long-range continuing study rather than one with a specific end, except possibly in specific cases.

It should be pointed out, however, that if research on the identification of degradation products as in Sec. 4.2.3 is undertaken, it could be considered part of this study as well, for it would go a long way toward identifying the basic reactions and their mechanism.

E4.3.3 Chemical Effects of Pollutants on Record Materials.

This study involves the reactions that occur between pollutants and record materials as well as their rates and mechanisms. Again, this is important for the prediction of lifetime in the presence of pollutants and for the development of accelerated aging procedures.

It will be noted, however, that a part of this information will have been developed if the research programs described in Secs. 4.2.1 and 4.2.2 are pursued, for carrying out those programs involves the reaction rate constant of pollutant with both wall and record materials. The present study could be considered an extension of that work to more pollutant/material combinations, and carried out in more depth.

E4.3.4 Accelerated Aging by Pollutants.

As was seen in Sec. E3, very little work has been carried out on accelerated aging in the presence of pollutants, yet it is an important area if the effect of pollutants is to be known in a quantitative manner. As in the development of all accelerated tests, the mechanisms and activation energies of the various reactions should be determined, as well as, ideally, their relationship to the physical measures of degradation. Some of this information would have been developed if the work carried in the previous section and in Secs.E4.2.1 and E4.2.2 is carried out. Nevertheless, to carry out such a program properly will be a long effort, albeit a worthwhile one. However, it is also possible to proceed more empirically. Thus, having chosen a record material-pollutant combination, the effects of concentration, temperature and humidity could be investigated. The problem here would be in the relationship of the results of such an investigation to performance in service. There really is no way to do this without a comparison of the experimental results to service results as was done for paper. However, such an empirical study could permit the <u>relative</u> ranking of pollutant/material combinations. The whole question of sealed tube aging naturally arises in this study, for moisture will have a profound effect, and such aging again brings up the question of degradation products.

E4.4 Summary and Conclusions.

The research program laid can be grouped into seven elements,which may be listed as follows.

1. Microenvironment and reaction in a container with inert walls.

2. Microenvironment and reaction in a container with reactive walls.

3. Identification of degradation products.

4. The "Book Problem" and folders.

5. Relation of basic degradation reactions to physical measures of degradation.

6. Chemical effects of pollutants on record materials.

7. Accelerated aging with pollutants.

This program would, in our view, go a long way toward carrying out the recommendations of the NAS Committee, and go beyond them them in developing the effect of pollutants on lifetime in service. Setting priorities among the elements of such a program requires a set of criteria, and many different orderings can be achieved depending on those criteria. Using the criteria of relevance to the problem of microenvironments in containers and the probability of achieving significant results we would place the elements of the program in the following order: 2,3,1,7,6,5.
Element 4 is omitted for the reasons given in the previous section. Element 6 is low on the list because a lot of the information that would be developed in this element would be developed in carrying out elements 1 and 2. Element 5 is low on the list despite its importance because it should really be considered to be a continuing background research effort and probably would have only long-term impact. Elements 1 and 2 are obviously central to the problem of containers and their utility, and element 3 is central to the problem of sealed, impermeable containers. Element 7 is placed where it is because of the importance of predicting performance in service in the presence of pollutants. Finally, it should be realized that this is a subjective listing based upon one set of criteria. Other criteria would very likely lead to another ordering.

Acknowledgements

The author is pleased to acknowledge gracious, courteous and uniformly helpful discussions with Professor Norbert Baer, Professor Glen Cass, Mr. Peter Waters, Dr. Charleton Bard, Dr. Chandru Shahani, Mr. W.K. Wilson, Dr. Leslie Smith, and Dr. Alan Calmes and the rest of the NARA staff.

TABLE OF CONTENTS

1. INTRODUCTION

The National Archives and Records Administration stores an enormous volume of records, and protecting them from degradation is a matter of great concern. Because the temperature and the condition of the atmosphere in the storage areas are important in controlling the rate of degradation of the stored records, these areas (the "stacks") have temperature and humidity control. However, atmospheric pollutants such as particulate matter, NO_x, SO_2 and ozone cause degradation of records, (see, e.g. reference (1)), and while in some cases the removal of air pollutants from the external air by the NARA air conditioning system is efficient, in other cases it is not (2), with the result that the concentrations of SO_2, and NO_x in the stack atmosphere are above recommended levels (3,4).

However, in the stacks, records (with the exception of books) are stored in containers, and not exposed directly to the ambient environment. The records experience a "microenvironment" which is possibly less aggressive than the macroenvirenment of the stacks. Certainly the use of containers protects the records from particulate matter. If this microenvironment in fact is, or could be made to be, less aggressive, then expensive changes in the air conditioning system might be obviated. For this reason, and because of the intrinsic importance of the topic, a National Academy of Sciences committee convened specifically to study the problem of the preservation of records, made the following recommendation(4):

> NARA should conduct a study of archival containers and microenvironments, including boxes, folders, and polyester encapsulation, with a view to understanding the maximum benefit that can be obtained from particular materials and designs. The committee feels that this is an unexplored area that may yield results highly significant to NARA's preservation efforts.

This report will analyze what is involved in a research program to carry out that recommendation. Following an analysis of the microenvironments experienced by stored records (principally in containers), which is the body of the report, a discussion of the ability to predict useful lifetimes from data on air pollution will be given. Finally, there will be laid out a suggested research program responsive to the recommendations of the NAS committee, and which can provide information on the basis of which NARA can make informed judgments about what actions to take to further their protection of historical records. The main body of the report is concerned with air pollutants. Temperature and water vapor microenvironments are treated in a separate Addendum.

The plan adopted to arrive at a research program was to model the environment inside a container, and to predict what changes occur in that environment when changes occur in the exterior environment, always remembering that the function of a container is protection from harmful substances in the ambient atmosphere. An analysis carried out by such models can outline the important features of materials of construction and of container design in a qualitative or semi-quantitative manner, and hence lead to two important conclusions: The important elements that should be included in a research program, and the type of protection that containers can provide.

2. MODELS AND MICROENVIRONMENTS

2.1 Introduction

Unless containers are hermetically sealed and constructed of impermeable materials (the document cases for the Constitution and the Declaration of Independence are outstanding examples of such cases) they will continue to exchange material between their interiors and the exterior environment via the gas phase. This may be thought of as a "flow" into and out of the container. If these flows were known, then the sophisticated modelling methods used by Cass and others (5,6,7) could be used to predict the rate of reaction of the contents of the container (i.e., the stored documents) with components in the environment. This presumes, of course, that the reaction rate constants are known, and as will be seen later, they generally are not. Moreover, even if these were known, it would still be necessary to relate this reaction to some measure of degradation. This subject will be discussed more fully in a later section of the report.

In the present case, the flows into and out of the containers are not known. Moreover, the flows are influenced by reactions with the contents, and, very importantly, the wall materials and construction of the containers. Hence, an integral part of the characterization of microenvironments and the reaction rate with pollutants of documents inside containers is the determination of flows into and out of containers. Note that "flow" need not be a gross macroscopic flow of material, but can be permeation, or diffusion.

A container can exchange material with the ambient environment by three distinct mechanisms:

1) Diffusion through the walls of the container.
2) Diffusion through any openings or gaps in the container walls.
3) Pressure and temperature driven flow through openings or gaps in the container walls, this mode can be thought of as "breathing".

Each of these mechanisms will treated, although not in every model presented.

2.2 Data and the Validity of the Calculations

In what follows, a number of rather complex calculations, with numerical results will be presented. These numerical results require such input data as diffusion coefficients, solubilities, and reaction rate constants. Data for these quantities are largely unavailable, and have had to be calculated or deduced from published material. (In fact, if they were known, the task of NARA would be largely finished.) As a result, while detailed calculations will be presented, it must not be assumed that these represent quantitatively what actually occurs, even allowing for the imperfect relation between a mathematical model and reality. But, while the results may not be quantitatively correct, it is believed that the principles illustrated will be correct. Moreover, it must be remembered that there is no substitute for experimental data. A model should not be believed without experimental verification. On the other hand, an experiment without analysis (often on the basis of a model) has little utility outside the specific experimental situation employed.

2.3 The Prototype Container

The NARA has a very large number of containers of various sizes and shapes used to store records--documents, films, tapes, etc. Each of these has a specific geometry and is made of a specific material. As will be seen, both of these factors influence the exchange of material between the interior and exterior of the container. To model individually each of these containers would be beyond the scope of this study, and is, moreover, not necessary to obtain the general principles that are of concern in this study. The general results obtained with one container can be translated fairly directly to another, provided the materials property data and dimensions are known. As a result, a prototypical container was chosen. It is style F in the NARA specifications for archival boxes (8).

This container (or "box" in the NARA specifications) will be used as a basis for calculations. It is generally filled with paper documents of legal size (8½"x14"). Hence, the system used for illustrative calculations will be paper-SO_2. If the data are available for other systems, the results should be easily translatable.

There are several important dimensions of the container. These are the total volume, the volume occupied by the contents, the unoccupied volume, the area of the surface through which atmospheric components may diffuse into and out of the container, and the thickness of the wall. Of crucial importance are any gaps or openings in the container walls, for the rate of diffusion in the gas phase is enormously greater than in the solid phase of the walls. Diffusion constants in the gas phase are of the order of 0.2 (9), while in the solid phase they are of the order of 10^{-9}. Hence, while gaps may be small in area, they can be crucially important as a pathway for communication between interior and exterior. Moreover, gaps are the means by which material is exchanged by the "breathing" modes discussed above.

An inspection of two boxes provided by NARA showed a number of gaps. These were on the bottom of the sides; between the hinged cover and the side walls; behind the hinged cover on the front; and at the edges behind the edge stay. Some of the gaps may be covered up when the boxes are on shelves in the stack, so it is difficult to estimate precisely the area through which diffusion can take place, and the length of the diffusion path. For the purpose of illustrating the importance of gaps, the gap behind the hinged cover in the front of the box was considered to be the only gap.

The important dimensions of this prototypical box are given in Table 1. These dimension are for an isolated box, not one crowded on a shelf. For the calculation of the area, the bottom was omitted. If the box were crowded on a shelf, the area of the front and back would have to be omitted, since these would not be accessible to the exterior atmosphere. What effect this has will be discussed at the appropriate points when the results of the calculations are presented. The thickness was taken as constant over the whole surface of the box, despite the fact that there are two thicknesses on the upper portion of the box on the sides. The reason for this is that the space between the cover and the sides is easily accessible to the exterior atmosphere.

2.4 Approximations in the Treatment

As will be seen in the next sub-section, the solution of diffusion problems forms a large part of this study. Diffusion, and its twin, heat conduction, are old and well established branches of physical science (10,11,12). The mathematical basis of the theory is well founded and, for our purposes, there are no outstanding basic questions. However, the application to specific situations can be mathematically very difficult, so two basic approximations have had to be made. First is the question of geometry. In its pure form, the problem of flow into a box is a three dimensional problem. To solve such a three dimensional problem for all the cases that will be considered would be extremely time consuming, if possible at all analytically. As a result, all the diffusion problems have been converted into one dimensional problems, as will be discussed when the specific models are analyzed. It is felt that this is not a serious approximation.

The second approximation is the assumption that diffusion constants are independent of concentration. The basic differential equations for diffusion with concentration dependent diffusion constants are, of course, well known, but their solution generally requires numerical computation. This might be appropriate for the solution of a well defined and important specific situation, but is not appropriate for the broader based treatment required for the present study. Moreover, in the specific cases when the diffusion of an air pollutant in polymers has been studied (13), the diffusion constant differs by about a factor of two with concentration. Considering that we have essentially no data on the diffusion of pollutants through paper, taking the diffusion constant to be independent of concentration is not unwarranted.

Another topic is not exactly an approximation, but nevertheless merits discussion. This is the treatment of the walls of the container as diffusing membranes. If the walls are polyethylene or polyethylene terephthalate, this would hardly be questioned. Such homogeneous plastic films are customarily treated in this way. The same is done in this report for the paperboard walls of the prototype container and paper in other forms as well. Paper is,of course, not a physically homogeneous material, so this may seem inappropriate. However, a permeability coefficient may be defined and measured for paper, as well as a solubility for various gases and vapors. That is all that is necessary to define a diffusion constant, so in this report paper and paperboard will be treated as a diffusing membrane.

Finally, there is the question of the solubility of pollutants, specifically SO_2 and NO_x, in the material of construction of the containers, and in the contents. The relation between solubility in the substrate and in the gas phase is assumed to be proportional. As above, the state of knowledge in the field and the mathematical complexity that would otherwise result make this a warranted assumption.

Definitions of the various symbols used, along with their dimensions and units, which can often be a vexing problem since various conventions are found in the literature, are given in Appendix A-1. This appendix also contains a discussion of a materials balance problem that is important in some of the models that are considered.

Even with these simplifying assumptions, exact solutions to specific diffusion problems are often quite complex and require computer methods for numerical calculation. Where possible, these exact solutions are given for the sake of completeness and because they might be used in subsequent work. In all cases, when the exact solutions are too complex, simplified solutions are obtained and used for numerical calculations. The simplifications are described at the appropriate places in the text.

With this introduction, we are now ready to analyze specific models which, it is felt, are important to understand if a rational subsequent program of study is to be developed. In each case mathematical details are relegated to and Appendix. The body of the text will describe the models, their importance, and discuss the results.

2.5 Flows Into an Empty Container or a Container Holding Inert Materials.

This is the simplest model that can be devised. It is useful for orientation purposes, and to provide the relative importance of the three mechanisms of flow into and out of the container already described. To recapitulate, these mechanisms are:

1) Diffusion through the walls of the container.
2) Diffusion through gaps or openings in the walls of the container.
3) Flow through gaps or openings in the walls driven by temperature or pressure changes--the "breathing" modes.

The first two are both diffusion modes, and will be described first.

2.5.1 Diffusion Modes

2.5.1.1 Constant Exterior Concentration

For this purpose, consider a container which is empty, or contains inert, unreactive material. Then consider a certain pollutant, e.g. SO_2. If the concentration of this pollutant inside the container is different from the outside, the pollutant will diffuse through the container walls or through gaps in them until the concentrations on the inside and outside are equal. The pollutant will always flow from the region of high concentration to that of low. The problem addressed is the following: "If the concentration inside the container is a given value different from the outside, and the latter is constant, how does the interior concentration change with time?"

First, this problem is changed into a one dimensional problem, i.e., diffusion is in only one direction ("inward" if the outside concentration is higher, "outward" if the outside concentration is lower.) How this is done is shown in Fig.2. The container is replaced with a chamber with all its walls but one impermeable. That wall consists of a permeable membrane representing the walls of the container, or gaps in those walls, as the case may be. The area, A, of this membrane is equal to the appropriate area in Table 1, and its thickness, ℓ, is the same as the thickness of the walls, or the diffusion length in the case of a gap in the walls. The membrane has a diffusion constant D. The container has an occupied volume V_c and an open volume V. The concentration of pollutant inside the container is C_1, which is a function of time, while the outside concentration is C_2 and, for this model, is assumed constant. Inside the container, as an approximation, C_1 is assumed to uniform with respect to position (i.e., it is "stirred"), which is a reasonable assumption considering the rapid diffusion in the gas phase. In the membrane, the concentration is C and is a function of position and time.

The exact solution of this problem is given in Appendix A-2 and will not be repeated here. As shown there, the solution involves the roots of a transcendental equation followed by the solution of an infinite set of algebraic equations, which, however, can probably reduce to a set of three or four. It was felt that the time it would take to work with this exact solution (which would be significant since it involves computer programming) would not be wisely spent, so a simplifying assumption was made.

That assumption was simply that the concentration gradient of pollutant in the membrane is linear, i.e, changes linearly from its value on the inside to its value on the outside. This assumption is expected to very good for thin membranes and less good for thick ones, but in any case to give a reasonable semi-quantitative solution. With this assumption the equation for the rate of change of C_1 is easily solved. This is done in Appendix A-3. Because the derivation and solution are very simple, and illustrate the principles involved, they will be repeated here. The uninterested reader can jump immediately to the discussion following Eq. 7.

The flux of pollutant through the membrane and into the container, in amount/unit area/unit time, is given by Fick's first law of diffusion:

$$F = D \left.\frac{\partial C}{\partial X}\right|_{x=0} \qquad 1$$

where D is the diffusion constant, C is the concentration in the membrane, and the derivative is taken at x=0 (see Fig.2). For a linear concentration gradient, Eq.1 becomes

$$F = D \frac{C(\ell) - C(o)}{\ell} \qquad 2$$

where $C(\ell)$ and C(0) are the concentrations of pollutants in the membrane at $x=\ell$ and x=0 respectively, and ℓ is the thickness of the membrane. Now, this flux of material into the box will increase the concentration there, and this will be greater the greater the area of the membrane, and lower the greater the volume of the box. Hence we can write

$$\frac{\partial C_1}{\partial t} = \frac{AD}{V\ell} (C(\ell)-C(0)) \qquad 3$$

for the rate of change of concentration of pollutant inside the box. Now, for diffusion through a gap, $C(0)=C_1$ and $C(\ell)=C_2$, hence we get

$$\frac{\partial C_1}{\partial t} = \frac{AD}{V\ell}(C_2 - C_1) \qquad 4$$

For diffusion through the walls, more care is needed because C_1 represents the concentration in the gas phase, while C represents the concentration in the walls of the box. These must be related in order to proceed. For that purpose, we define the dimensionless distribution coefficient S (see Appendix 1) as

$$S=C_s/C_g \qquad 5$$

where C_s and C_g are the concentrations in the solid and gas phases respectively, and we assume that S is independent of concentration. With these changes the equation for diffusion through the walls becomes

$$\frac{\partial C_1}{\partial t} = \frac{ADS}{V\ell}(C_2 - C_1) \qquad 6$$

which is the same as Eq.4 except for the factor S.

As shown in Appendix A-3, the solution to Eqs. 4 and 6 is

$$C_1/C_2 = 1 - (1 - C_1^o/C_2) \exp(-t/\tau) \qquad 7$$

where τ is $V\ell/AD$ for diffusion through gaps and $V\ell/SAD$ for diffusion through walls, and C_1^0 is the concentration inside the container at time t=0, i.e., when the container is closed.

Equation 7 gives the ratio of the concentration inside the container to that outside as a function of time. This is plotted in Fig.3 for a value of $C(0)=0.1C_2$, i.e, at t=0, the concentration inside the container is just 0.1 that on the outside. The effect of choosing other values for this quantity will be discussed shortly. The values of ℓ,A, and V are from Table 1, so that this represents diffusion into that specific NARA box. Curves are given for values of diffusion constants of 10^{-8} and 10^{-9} and for full and empty boxes. The values of D come from an analysis of the data of Hudson and co-workers (14, 15,16), and will be discussed in a later section of the report.

In each case the curves start from the value of 0.1 (note that the very early times for the curves for diffusion through gaps are not shown) chosen for the initial conditions, and rise smoothly to the value 1, at which point the concentration in the box is the same as the concentration on the outside. As expected, it takes a shorter time for the full than for the empty box to reach this value. If a different initial concentration had been chosen, the curves would have risen smoothly from that value to the value 1, but the time over which the change takes would be the same. This is totally controlled by the parameter τ.

Most striking is the substantial difference between diffusion through gaps and diffusion through the walls of the box. Depending on the diffusion constant in the box walls, diffusion through gaps is 100 to 1000 times faster than diffusion through walls. Thus, for gaps, equilibration is essentially complete in one day or less, while for walls, for these diffusion constants, several months to more than one year are required. This striking effect of gaps will become even more apparent later.

The time dependence of this process is contained in the parameter τ of Eq.7. This serves the function of a "relaxation time" for the process, and values for the six curves are given in Table 2. It can be seen that the value of these relaxation times, which roughly represent the time scale over which changes take place, reflect the statements just made. The value of the relaxation time is determined by the geometry of box through V,A, and ℓ,and by the material of construction through D and S.

2.5.1.2 Exterior Conditions Vary with Time

The calculations presented in the preceding section were interesting and led to an important conclusion about the effect of openings in the box walls, but they were rather artificial in that they assumed the concentration of pollutant in the air outside the box was constant in time. This is, of course, not the case. The concentration of pollutants in the stack atmosphere is known to fluctuate (2), and, in the case of NO_x, to follow the diurnal variations in the ambient District of Columbia environment (2). Hence, in this section we answer the question, "What happens when the exterior concentration is not constant?" Recall that we are still dealing with an empty container or one filled with inert documents.

Again the process has to be modelled. For that purpose we consider that the concentration of pollutant in the stacks varies in the manner of NO_x as determined by Hughes and Myers (2). We further simplify this by assuming a sinusoidal variation with a period of twelve hours. A sketch of the assumed variation is shown in Fig. 4. It will be noticed that C_c is the average concentration and C_f is the time varying component. While this is a simplification, it should be mentioned that the methods of analysis to be described could easily be used for an accurate Fourier series representation of the actual time variation of the concentration. This was not done because the added mathematical complexity would not have added sufficiently to the insight gained from the simpler model adopted.

This model is solved in Appendix A-4. An exact solution could be obtained by the methods given in Appendix A-2, but this was not pursued because the mathematical complexity would have precluded its use in this study. Again the approximation of a linear concentration gradient in the walls or in any gaps was made, and the resulting expression for the time rate of concentration inside the container is

$$\frac{C_1}{C_c} = 1 - \left(1 - \frac{C_1{}^{\circ}}{C_c}\right) \exp\,(-t/\tau) + \frac{C_f}{C_c}\,\frac{\mathrm{Sin}(\omega t+\delta)}{1+\omega^2\tau^2} \qquad 8$$

This is the analogue of Eq. 7, and all other terms are the same as there and in Fig. 4, except for ω and δ . The former is 2π/period of the variation, and δ is given by

$$\tan\delta = -\omega\tau \qquad 9$$

Its meaning will be discussed in the next paragraph.

It will be seen by comparing Eqs. 7 and 8 that the latter is exactly the same as the former, except that it contains an added term which is sinusoidal. What this means is that the time variation of concentration is exactly as given in Fig. 3, except that there is added to the curves a ripple caused by the sinusoidal variation of the exterior concentration. The period of this ripple is the same as that of the exterior (i.e., twelve hours), and its magnitude is $Cf/Cc(1+\omega^2\tau^2)$. It is out of phase with the exterior fluctuation, the phase difference being given by the quantity δ, which essentially gives the time difference between peaks in concentration in exterior and interior.

The quantity that governs the magnitude of the interior ripples is $(1+\omega^2\tau^2)$. The τ are the relaxation times given in Table 2, and in Table 3 we give the values of $(1+\omega^2\tau^2)$. First we describe the situation with diffusion through walls. Here the values range from 48.7 to 20,000. Hence, in the worst case (a full box with diffusion constant of 10^{-8}), the amplitude of the ripple is about 1/50 of the exterior amplitude. This would hardly be visible on the graphs of Fig. 3. In the best case the amplitude is a totally negligible 1/20,000 of the exterior amplitude. Thus, for diffusion through walls, at least for the values of the constants chosen, the interior concentration rises smoothly from its initial value to the average concentration in the exterior with hardly a discernable ripple, as do the curves in Fig. 3.

The situation when a gap is present is far different. Then the value of $1+\omega_2\tau^2$ is essentially unity for both full and empty boxes. This means that the concentration inside the box is essentially the same as in the exterior. The ripple to be added to the appropriate curves in Fig. 3 has the same magnitude as the variation in the exterior. After the transient has died out (about one day, see Fig. 3), the interior environment is exactly the same as the exterior, and the box provides no shielding from the macroenvironment. Considering that the two relaxation times are approximately 25,000 sec. (7 hours) and 5600 sec. (1.5 hours) while the period of the oscillations is an assumed 12 hours, this is just what would be expected.

2.5.2 Breathing Modes

It will be recalled that breathing modes were the mechanisms by which the interior of a container could exchange material with the exterior by pressure and temperature changes. This, of course, requires gaps or openings in the walls of the container. To make clear the mechanism of these modes, consider pressure first. Let the atmoshperic pressure change. It is assumed that the container has rigid walls and that the pressure in it is always the same as the atmospheric pressure, air being drawn into or exhausted from the container to maintain this condition. For the purpose of visualization assume that the atmosphere has a concentration of pollutant higher than that in the container. When the atmospheric pressure increases, and assuming the temperature remains constant, air flows into the container. This air carries pollutant with it, and this will increase the concentration of pollutant in the container. Now let the atmospheric pressure decrease, again assuming constant temperature. Air will be exhausted from the container, <u>but this will not change the</u>

concentration. Repeat the cycle many times. Eventually the concentration in the container will the same as the exterior concentration, and any further cycling will not change it.

Temperature changes work the same way. Assume the atmospheric pressure remains constant. Now decrease the temperature. The only way a constant pressure can be maintained in the container with constant volume is for the amount of air in the container to increase. Hence air will be drawn into the container, changing the concentration. Conversely, as the temperature increases, air will be exhausted from the container, but again the concentration will not change. Eventually, the concentrations inside and outside the container will be equalized.

The problem we ask, with either of these mechanisms, is,"How does the concentration vary with time?" For this it is necessary to model the temperature and atmospheric pressure changes. The model that was chosen is shown in Fig. 5. Either of these two variables cycles, its value rising linearly from an initial value P_i or T_i to a final value P_f and T_f, and then drops linearly to the same initial value. Actually, it is not necessary that the rise and decrease portions of the cycle be linear, nor that they have the same length in time. All that is necessary is that they be monotonic.

The breathing model is solved in Appendix A-5. There it is shown that the ratio of the interior to the exterior concentration for pressure cycles is

$$\frac{C_1}{C_2} = 1 - \left(1 - \frac{C_1{}^o}{C_2}\right) \frac{P_i}{P_f}^{N} \qquad 10$$

where N is the number of cycles, and for temperature changes the completely analogous expression

$$\frac{C_1}{C_2} = 1 - \left(1 - \frac{C_1{}^o}{C_2}\right) \frac{T_f}{T_i}^{N} \qquad 11$$

is obtained. Note that i and f are interchanged in these equations. The reason is that air enters the container when the pressure <u>increases</u>, but enters when the temperature <u>decreases.</u> Note also that when N=0 (at the start of the process when the records are boxed), $C_1=C^1{}_0$. Now, P_i/P_f and T_f/T_i are both less than unity. Hence for very large N, $C_1=C_2$. Finally, it should be noted that the size of the box, its dimensions, and the materials of construction do not enter into these expressions.

To illustrate this behavior we assume that the atmospheric pressure varies with a weekly cycle, and that P_i and P_f are 29" H_g and 31" H_g, respectively. Similarly, for the temperature, a one day cycle with T_i=293K and T_f=292K, representing a temperature fluctuation of approximately two degrees Fahrenheit between night and day. A more accurate estimate obviously could be made using the stack temperature records.

The results are plotted in Fig. 6 on the same scale as Fig. 3 so as to make comparison easy. It is seen by comparing these two figures that the breathing modes are quite slow (at least for the conditions assumed here) and amounts approximately to the flow caused by diffusion through walls with a diffusion constant of 10^{-9}.

2.5.3 Discussion and Conclusions

The change of concentration with time inside a box has been calculated for diffusion through the walls and through gaps in them for constant and fluctuating exterior conditions. The breathing modes of the box have also been calculated. It has been found that for reasonable values of the diffusion constant and solubility in the walls, diffusion through gaps in the walls is by far the most efficient process for exchanging material between inside and outside of a container. This is the expected result given the values of diffusion constants in gases as compared to solids. Indeed, the calculations show that if there are significant gaps or openings in the walls, containers provide little, if any, protection from the outside environment, except possibly for protection from particulates

Even for diffusion through walls, the concentration of pollutant inside the box eventually reaches the level in the exterior, and hence it might be thought that containers provide no protection, at least for very long times. The next section will show that this is not the case. The reason is that the present calculations were for an empty case or one filled with inert materials. If the contents of the container are not inert but instead react with the pollutant, then their presence will affect the diffusional flow into the container. Moreover, they obviously cannot react more rapidly than material flows into the container, and thus the container can at least in principle provide protection. If, for example, the container were hermetically sealed and made of a material through which the pollutant cannot diffuse (e.g. glass or steel), then obviously complete protection would be provided. But then, as will be seen in a later section of the report, new and serious problems arise.

2.6 The Container With Reactive Contents

The problem that will be addressed in this section is that of a container that holds documents that react with the pollutant in question. This is clearly a more realistic representation of reality than the models of the previous section, for there would be no problem if the contents of the container were inert.

Again, however, assumptions about the situation have to be made if the model is to be solved with the resources available in the present study. Hence the following assumptions are made:

1. The contents react with the pollutants in a first order reaction.
2. The reaction is not diffusion limited; i.e., the rate of reaction is not limited by the rate of diffusion of pollutant into the records. This seems to be the case in the experiments of Lyth-Hudson and co-workers (14-16) on paper and SO_2, which is one of the principal systems of concern. These experiments will be discussed and analyzed in a later section of the report.
3. Because of the previous assumption, the contents are taken as loosely

packed, for if they were not, diffusion might be the rate limiting process.

An exact solution for this model is given in Appendix A-6. Again, this is given for reference only, and will not be considered further. An approximate solution, using the same approximation of a linear concentration gradient in the container as used in the previous section is given in Appendix A-7 for a constant exterior concentration of pollutant, and in Appendix A-8 for a fluctuating exterior concentration.

In this case there are two quantities that can be calculated: the concentration in the gas phase inside the container as a function of time, and the concentration of reacted materials in the container contents, again as a function of time. As shown in Appendix A-7 for constant exterior concentration the equation for the concentration is

$$\frac{C_1}{C_2} = \frac{1}{1+\tau_1/\tau_2} + \left[\frac{C_1{}^{\circ}}{C_2} - \frac{1}{1+\tau_1/\tau_2}\right] \text{exp.} \left[-\left(\frac{1}{\tau_1}+\frac{1}{\tau_2}\right)t\right] \qquad 12$$

and for the concentration of reacted material in the container contents is

$$C_r - C_r{}^{\circ} = \frac{kSC_2 t}{1+\tau_1/\tau_2} - \frac{kS}{(1/\tau_1+1/\tau_2)} \left[C_1{}^{\circ} - \frac{C_2}{1+\tau_1/\tau_2}\right] \times$$

$$\times \left\{\exp\left[-\left(\frac{1}{\tau_1} + \frac{1}{\tau_2}\right)t\right] - 1\right\} \qquad 13$$

All the quantities in these equations have the same meaning as in Eq. 7 of the last section, and V_c is the volume of records. However, care must be taken with the total volume, V. This represents the total volume available to the <u>unreacted</u> pollutant in the box. Now, as discussed in Appendix A-1, the unreacted pollutant can be in the gas phase, which is the unoccupied volume, or in solution in the contents, in equilibrium with the gas phase. The former is simply the volume of the empty space in the box. The latter is, however, SV_c, which can be quite large for large values of S. The sum of these is the volume V. In effect, this substantially increases the value of the relaxation times as compared to the treatment in the preceding section. There are now, moreover, two relaxation times. The first, τ_1, pertains to diffusion through the walls or gaps in them, and, as before is given by $V\ell/ADS$. The second, τ_2, pertains to the rate of reaction of the contents with the pollutant, and is given by $V/V_c kS$, where V_c is the volume of contents, and k is the first order reaction rate constant. The behavior of the concentration in the gas phase will be discussed first.

As compared to the situation with inert contents, there is an important and significant difference in this case. In the previous case, for very long times, the concentration in the gas phase was just equal to the exterior concentration, and diffusion of pollutant into the container stopped. In the present case, for very long times the concentration in the gas phase approaches the value

$$\frac{C_2}{1+\tau_1/\tau_2} \qquad 14$$

Thus, since both relaxation times are positive quantities, the interior concentration is lower than the exterior. Hence diffusion into the container cannot stop. The rate of diffusion of pollutant into the container is just balanced by the rate of reaction with its contents, thereby keeping the concentration constant at the value given above.

To demonstrate the behavior of the concentration in the gas phase as a function of time, a graph was made from Eq. 12, and is shown in Figs. 7 and 8 for diffusion through walls and diffusion through gaps, respectively. The parameters for the calculations are given in Table 4. For this case, the container was assumed to be half full so that the document sheets are relatively loosely packed and the assumption that the rate of reaction is not diffusion limited could be justified. Otherwise, the container is the prototypical box. The most important parameter, however, is the reaction rate constant. These are values that were calculated (or deduced) from the previously mentioned work of Hudson and his collaborators(13-16) as will be discussed later in a separate section of the report. In this work, the "uptake", or sorption, of SO_2 by paper was studied. The conclusion was reached that sorption of SO_2, which remained mobile, was followed by conversion of the SO_2 to SO_3, which was then fixed, and presumably catalyzes the degradation of the paper. The reaction rate constant refers to this conversion, not necessarily the degradation, as will be discussed later when the degradation of paper is addressed. Two values are chosen from the values deduced, a low one calculated for pure rag paper, and a high one calculated for newsprint containing a high percentage of ground wood. Whether the numbers are correct or not, they at least ought to have comparative meaning and to illustrate the principles involved. The value of k for the pure rag paper was calculated to be 2.9×10^{-8} and for the groundwood paper the substantially higher value of 830×10^{-8} was calculated.

For all the various curves to be presented, the initial concentration of pollutant in the gas phase was assumed to be the same as the exterior concentration, and the paper was assumed to be in equilibrium with this. This seems a reasonable assumption--indeed, more reasonable than others which could be made. The diffusion constant was taken to be 10^{-8} for all the curves, to keep the number of results manageable.

Figure 7 gives results for diffusion through walls, and Fig.8 for diffusion through gaps, and in each case the ratio of the interior to the exterior concentration is plotted as a function of time, with time on a logarithmic scale. Referring first to Fig. 7, the curve for the pure rag paper drops smoothly from a value of unity to a value of 0.56, but requires more than a year to do so, while that for the groundwood paper drops to the very low value of 0.0044 in about a week. Clearly, during the earlier times the paper is reacting with the pollutant in solution in the paper and the much smaller amount in the gas phase. The concentration decrease represents the fact that diffusion through the walls of the container cannot keep up with the rate of reaction and the concentration inside the container must necessarily drop, but this takes longer for the less reactive paper. In this sense the reaction is diffusion rate limited, but the diffusion is that through the wall of the container and not into the documents. The final concentration for the more reactive paper is lower than for the less reactive paper, which is what is to be expected. These results show that sealed boxes can provide protection, a result that will become even more evident when the results for the concentration of reacted species in the paper are discussed.

In contrast with these results are the results for boxes with gaps. These are given in Fig. 8. Here the results are strikingly different. For the less reactive pure rag paper, the concentration in the gas phase maintains its initial value, which is the same as the exterior concentration. For the more reactive groundwood paper, the concentration drops within one hour to a value only about 0.93 of the exterior concentration. In both cases, diffusion through the gaps just about keeps up with the rate of reaction. For all practical purposes the box provides no protection from the pollutant.

These results are corroborated and made more meaningful when the concentration of reacted material in the box contents is calculated. This is given by Eq. 13, and is plotted in Figs. 9 and 10. Note that both these figures are on a log-log scale to make the results more evident. Consider first Fig. 9, which is for diffusion through walls. This figure contains two straight lines which represent the situation when the documents are not in a container. Consider now the case when the container holds the less reactive pure rag paper. At first, for about a year, the change of concentration of reacted material follows the curve for paper outside the box. Then the reaction rate decreases and in about a 5 years becomes linear again, and the concentration of reacted material is about 0.7 what it would have been in the absence of a container. Diffusion through the walls can just about keep up with the rate of reaction. The behavior of the more reactive groundwood paper is the same, but far more pronounced. Thus, for somewhat more than an hour, the change in concentration of reacted material is the same as would occur in the absence of a container, but then, in the period of about a year, the reaction drops and eventually becomes linear again. However, recall that this is a log-log plot. What this means is that the concentration in this case when it reaches the steady state condition is less than 1/100 what it would have been in the absence of a container, and remains so as time goes on. This, then, represents the maximum protection that can be provided by a sealed box with the various values of the parameters for box and contents we have chosen, and, of course, based on our model. Diffusion through the walls can just about keep up with the rate of reaction of the slowly reacting paper, but not with the fast. The rather obvious conclusion is that if the diffusion constant or the solubility coefficient for the walls were zero, then there would be no reaction after all the pollutant in the gas phase and in solution in the contents was used up. The formalism predicts this obvious result, but also gives what happens when this limiting condition does not obtain.

Consider now what happens when there are gaps in the box. The results for this case are given in Fig. 10. Here the curves are very simple. For both the pure rag and the groundwood papers, they are essentially linear on the log-log scale representation. Moreover, a comparison of these curves with the lines representing the unboxed papers in Fig. 9 shows that the concentration of reacted material in the contents of the box with gaps is essentially the same as for the unboxed papers. We are forced to conclude from these results, and from this rather simple model (which of course needs experimental verification) that boxes with gaps of the size we have assumed provide little if any protection from a reactive environment. The microenvironment is practically the same as the ambient macroenvironment.

Having investigated the case with reactive contents for a constant exterior concentration of pollutant, we now investigate the case of a fluctuating external concentration. This is carried out in Appendix A-8, but the exact solution (which could very likely be carried out by the methods in Appendix A-6, but would certainly be quite complex) is eschewed. The approximate solution proceeds as in Appendix A-4, and the result is

$$\frac{C_1{}^{\circ}}{C_c} = 1 - \left(1 - \frac{C_1{}^{\circ}}{C_c}\right) e^{-t/\tau_s} + \frac{C_f}{C_c} \frac{1}{(1+\tau_1/\tau_2)} \frac{\mathrm{Sin}(\omega t+\delta)}{1+\omega^2\tau^2} \qquad 15$$

Again, because of the factor $1+\omega^2\tau^2$, the sinusoidal term is negligible for the case of diffusion through walls, and is present for the case of diffusion through gaps. Moreover, in calculating the amount of reaction, this term causes some analytical difficulties, hence this matter was not pursued. The conclusion is the same as before: It adds a minor perturbation to the case of diffusion through walls, and for the case of diffusion through gaps changes the microenvironment somewhat, but not significantly.

2.6.1 Discussion and Conclusions

The most significant conclusion from this section is that containers can provide protection from the macroenvironment, but provided they are sealed and have no gaps in them. The reason for this is that the presence of reactive material in the container substantially changes the environment inside the container, and serves to reduce the level of pollutant inside the container. The rate of reaction then becomes very strongly dependent upon the rate of diffusion of pollutant through the walls of the container, and if this is low, so will be the reaction rate. The obvious conclusion, already mentioned, is that if the diffusion constant is zero, i.e., if the container is hermetically sealed, and the walls are impermeable, after a while reaction will cease. However, as will be seen later, other problems may arise.

The question naturally arises, "What happens if the container walls react with the pollutant?" This is perhaps the most important of all the cases studied, and will be taken up next.

2.7 The Container With Reactive Walls

2.7.1 Introduction

Having treated containers with inert contents and with reactive contents, this section investigates containers with reactive walls. Of the various cases investigated, this one appears to be the most promising for the protection of documents. The reason for this is easy to see. If the container reacts with the pollutant as the pollutant diffuses through it, then the pollutant may never get into the container, or perhaps only a small amount may get through, depending on the extent of reaction. In due course, the container may be destroyed, but the documents would have been protected. The container is sacrificed to save the contents, much as is a sacrificial anode in corrosion protection.

Indeed, this may already be the case with at least some of the NARA containers. Archival storage boxes of the type we have chosen as the prototype container for this report already are specified to contain 3% $CaCO_3$ (8). Every person we have consulted on this project has remarked that SO_2 and NO_2 would react with the $CaCO_3$ in their passage through the walls. Indeed, SO_2 is known to react with limestone, probably forming $CaSO_4$ (17), and ozone would probably react even with wall material that does not contain an additive. The fate of NO is not known, nor is the fate of other pollutants. However, it might be hypothesized that acidic components that might be in the atmosphere might also be removed by the $CaCO_3$, and thus provide protection from these as well.

This section investigates two models of containers with reactive walls: one an empty container, and the other a container with reactive contents. Unfortunately, these are substantially more difficult problems than those previously treated, so only a limited treatment can be given. However, even this more limited treatment illustrates the principles involved.

In what follows, it is assumed that there are no gaps in the container walls. Clearly, if the pollutant can diffuse or flow through gaps, then it cannot react with the container walls. However, even in this case, the reactive material of the walls may provide some protection. This will be discussed in the discussion portion of this section.

2.7.2 The Empty Container

As already mentioned, the analysis of diffusion into a container with reactive walls is a substantially more difficult problem than one with inert walls. The reason for this is that there is an added term in the basic diffusion equation, representing the fact that as a material diffuses it also reacts. As before, it is assumed that this reaction is first order. This somewhat simplifies the problem, but it is still difficult. Nevertheless, a formal exact solution is sketched out in Appendix A-9. The model is the same as in Appendix A-2, except that the pollutant now reacts with the walls with a first order reaction. The solution was not used because of the reasons previously given, and is presented here because of the importance of the problem, and because it might be used in future work. Even such a formal solution does not appear to exist in the literature.

Appendix A-10 gives an approximate solution to this case and to the case of a container holding reactive documents. The approximation used here is more restrictive than the one used previously of a linear concentration gradient. It was felt that the use of that approximation with reaction as well as diffusion taking place in the walls would not be realistic, so the problem was solved only at steady state, i.e., after sufficient time has passed that the system no longer shows any time dependence. This approximation was previously used by Odian and Kruse (18) in a somewhat simpler context, and corresponds to Eqs. 7 and 12 with the exponential term missing. For an empty container (or, as before, for one with inert contents) the solution for the flux of pollutant into the container is

$$F = (Dk)^{1/2} \frac{SC_2 - C_1 S \text{ Cosh } r\ell}{\text{Sinh } r\ell} \qquad 16$$

where all the terms have the same meaning as before and r is defined in Appendix A-10. Now, by hypothesis, the exterior concentration, C_2, is constant, and since this solution is for steady state, the interior concentration, C_1, must also be constant. This can only happen if something inside the container is consuming the pollutant at just the rate at which it is flowing into the container, or if the flux into the container is zero. The latter is obviously an important result, and the condition that it obtain is given by

$$C_1/C_2 = \frac{1}{\text{Cosh } r\ell} \qquad 17$$

This interesting result gives the relation between the interior and exterior concentrations for the flux of pollutant into the container to be zero. Note that the relation depends upon k, D, and l. For a given value of the exterior concentration, the interior concentration for zero flux into the empty container decreases as k and ℓ increase, and as D decreases. This is accord with expectation.

What this relation means is as follows. At the interior boundary of the container wall, pollutant will flow out of the wall and into the container. However, pollutant will also diffuse into the wall from the atmosphere inside the container. The relation gives the condition that these two flows be equal.

Table 5 gives some values of the ratio of C_1/C_2 for the prototype container. Unfortunately we have no values of the rate constant k for paper containing $CaCO_3$, so we have used values calculated from the data of Hudson, et.al. (14-16). Recall that the lowest values of k were for rag paper, and that the highest values were for paper containing groundwood. These calculations are obviously for illustrative purposes only, but the enormous range of values of the concentration ratio should be noted. This comes about because of the exponential character of the hyperbolic cosine.If these values are correct, then it could be concluded that even boxes made out of groundwood would be effective in protecting contents, but this would be a very bad error, for in that case, other and serious complications arise.

2.7.3 The Container With Reactive Walls and Reactive Contents

This model is also solved in Appendix A-10. The result for the ratio of the interior concentration to the exterior is

$$C_1 = \frac{C_2}{\frac{Vc}{A}\sqrt{\frac{k_c}{Dk_w}}\ \mathrm{Sinh}\ r_w\ell + \mathrm{Cosh}\ r_w\ell} \qquad 18$$

where k_w and k_c are the reaction rate constants for the walls and the constants, respectively, for they need not be constructed of the same materials. Again, numerical results were calculated as in Sec. 2.6 for the same conditions as in that section and for the four possible combinations of the two rate constants used there. Now, since the rate of reaction is proportional to the concentration, this is the same as the ratio of the rate of reaction of contents inside the box as compared to what it would be in the absence of a box. Hence, within the limitations of the model, it represents the degree of protection provided by a box with reactive walls, and, of course, is the microenvironment inside such a box. It is important to note that the results are dependent upon *both* the walls and the contents. They act together. The ratio for a box made of rag paper filled with rag paper contents is 0.09, while for the groundwood-groundwood combination is a totally negligible 10^{-9}. Again, this should not be read as meaning that archival boxes should be made of groundwood, for then, as will be discussed later, other serious problems arise. What the results indicate is that if the walls of the box are constructed of a material that has a rate constant for reaction with pollutant of the value we have chosen for groundwood *and all other things are equal*, then the protection, again within the limitation of the model and the approximate nature of the analysis, will be as indicated by the results in Table 6.

2.7.4 Discussion and Conclusions

This section has shown that a *sealed* box (no gaps) constructed of reactive material can provide essentially complete protection from pollutants provided that the box walls can react with the pollutant. Again, this is a rather obvious result, but the means for the calculation of the amount of protection provided are given, at least for a simple case.

The case with gaps merits some discussion. Generally speaking, gaps will "short out" the walls and hence preclude the protection provided by the walls if they are reactive, as in this model, or even if they are not, as in the previous model. However, as pointed out to us by Professor Cass, this need not be the case. If the gap has a long enough diffusion length, then as the pollutant diffuses through the gap, it will also diffuse to the walls of the container. There, if the walls are sufficiently reactive, it can react with them and thereby be prevented from diffusing into the container. This mechanisms merits further investigation.

2.8 The Book Problem

As mentioned in the Introduction, books are not generally stored in containers, although they may be sealed in polyethylene shrink wrap, or they may be stored in closed book shelves. Whether they are so stored, or are stored on open shelves, there is a problem of the mechanism by which pollutant attacks the book pages. The problem is simply stated: "Does the pollutant diffuse in through the edge of the sheets or does if diffuse in between the sheets and then spread laterally?" It will be clear that this applies to documents contained in folders as well. It will also be clear that the looser the sheets are packed, whether in a book or a folder, the more likely is diffusion to occur between the sheets and then spread laterally, because the diffusion constant in gases is so much greater than in solids. Because of its intrinsic importance this problem was investigated.

The "book problem" is a problem of diffusion into a laminate composite, but with diffusion occurring from the edge of the composite, not from the face, as is usually considered. There are two published exact solutions for the temperature distribution for heat flow from the edges of such composite laminates (19,20), one for constant temperature boundary conditions, and the other for time varying boundary conditions. Such heat flow problems can generally be converted into diffusion problems, but this was not done in this case because of the complexity of the solutions. Rather, a simpler approach was taken.

There is a well known phenomenon in metallurgy known as "grain boundary diffusion." The boundary between grains in a polycrystalline metal is known to have a much higher diffusion constant than the region in the grains. Hence when diffusion occurs in a polycrystalline metal, the diffusing material travels down the grain boundary and then spreads laterally into the grain. This is similar to the book problem, with the space between the sheets taking the place of the grain boundary.

There are two well-known solutions of the grain boundary problem (21,22). The first of these, by Fisher, is easier to apply and was the one used for this report. Using the terminology for the book, it gives the ratio of the concentration inside the book to the exterior concentration as a function of the distance from the edge of the book sheets (y), and from the center of the position between sheets (x). The result is

$$\frac{C_1}{C_2} = \exp \quad - \frac{\sqrt{2}y_1}{(\pi t_1)^{1/4}} \quad \operatorname{erfc} \frac{x_1}{2\sqrt{t_1}} \qquad 19$$

with the following definitions:

$y_1 = y/\delta(D'/D)$
δ = Thickness of the inter-sheet region
D' = Diffusion constant in the inter-sheet region
D = Diffusion coefficient in the sheet
$t_1 = Dt/\delta$
$x_1 = x/\delta$

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-z^2} dz$$

From this, knowing the values of the various constants, the concentration profile for the pollutant within the book sheets can be calculated.

In order to apply this, the thickness of the inter-sheet region must be known. This will, of course, be dependent on how much pressure is applied to the book, or alternatively, how tightly the book is packed on shelves. To get some idea of what this might be, a very rough experiment was carried out. Ten books from the author's library were measured. The thickness of the sheets was measured, and the thickness of the book was measured (excluding the covers), using an eleventh book as a "standard weight". It was found that, on average, the thickness of the book was approximately 10% greater than the sum of the measured thickness of the sheets, with values ranging from 6% to 16%. Sheet thicknesses varied from 0.0078 to 0.016 cm. These, of course, must be considered to be very crude measurements.

The most serious problem in carrying out a calculation is the value of the inter-sheet diffusion constant, D'. It would be expected that its value would be lower than the value for air and higher than the value for diffusion in the sheet material, but where in this enormous range the value might actually lie is hard to determine. Nevertheless, in the nature of an exploratory calculation, its value was taken as that for diffusion in air, namely 0.2 cm^2/sec. The concentration profile was calculated for a diffusion time of one day, with the following values of the other parameters: =0.001 cm; D=10^{-8} cm^2/sec; sheet thickness=0.01 cm. The results are shown in Table 7, which gives the concentration ratio as a function of the distance from the edge of the sheets at the position between the sheets and at the center of the sheets.

The results are totally contrary to experience. They show that if the diffusion constant in the inter-sheet region were that in the gas phase, after only one day or so, the whole book would be permeated by pollutant. The brown discoloration commonly observed around the edges of book sheets (increased by lignin, hemicellulose, resin and and trace metal ion content of the paper(25)), would instead be uniform over the sheet. To the extent that these very crude results have any meaning, they indicate that the diffusion constant between sheets is more nearly that for diffusion in the sheets than it for diffusion in the gas phase. The whole book acts almost like a block of solid paper. The inter-sheet region is very likely a quite complicated thing, perhaps corresponding to diffusion through a percolation maze.

On the other hand, the results do indicate that if sheets are loosely packed, then the high diffusion constant in the gas phase assures that they quickly become permeated with pollutant, an assumption that was used in some of the models.

2.9 An Analysis of the Data of Hudson and Co-workers

In a series of three papers (14-16), Hudson and co-workers studied the "uptake" (sorption) of SO$_2$ by papers of various kinds. These workers found that the sorption processes could be divided into two steps: a relatively rapid process that lasted for 24-48 hours, in which it was hypothesized that the SO$_2$ was going into solution in the paper fibers or adsorbed on the surface of other substances present in the paper, and a much slower irreversible one in which the SO$_2$ was "fixed", presumably by conversion to SO$_3$ and thence to sulfate ion. This latter process continues indefinitely with a rate that is strongly dependent on the type of paper. The rate was shown to be accurately linear for periods of up to six months, and to be proportional to the square root of the

SO_2 concentration in the gas phase. The concentrations were 10 ppm and higher. In the words of Edwards, et.al.,(15),

> A detailed consideration of the processes that are likely to be important in the sulfur dioxide-paper system show that the sulfur dioxide present in the paper may be held in two ways, i.e., "reversibly" and "irreversibly".
>
> The reversibly sorbed sulfur dioxide is in equilibrium with the sulfur dioxide in the gas phase. It most probably corresponds to sulfur dioxide "dissolved" in the cellulose/water matrix plus the sulfur dioxide (or "sulfite" ions) physically sorbed at the surfaces of the inorganic oxide fillers or other polar solids present in the paper. It may be noted here that not only would this equilibrium be attained in 24-48 hours but also that the total quantity of sulfur dioxide sorbed in this way within such a short period may well correspond to almost the total sulfur dioxide content of the paper.
>
> Only the irreversibly held sulfur dioxide would appear to be important in the context of the build up of acid in the paper. It probably corresponds to sulfate ions (i.e. the oxidation products of sulfur dioxide or sulfite ions), and to sulfonic acids, the latter associated with the lignin content of the paper.

These were the best papers found in the literature that permitted at least a crude approximation to some of the constants necessary in the calculation of numerical results from a model. What is necessary to know are the solubility coefficient S, the diffusion constant D, and the reaction rate constant, k.

The first of these is easily obtained from the results at short times (24-48 hours). From the results as quoted, this corresponds to the solution and adsorption of SO_2. In the first of the three papers, results are given for two papers: a gelatine sized pure rag paper, and a rosin sized paper containing 60% groundwood and 40% chemical wood. For both papers, the amount of this reversibly sorbed SO_2 depended strongly on the relative humidity, with the sorption-Rh curve having a shape similar to the moisture regain curve. At 50% Rh, the sorption was about 200 ppm for the rag paper, and about 300 ppm for the other paper. In both cases the gas concentration was 10 ppm, so the values of S are 20 and 30, respectively. The value of 30 was used in the calculations. It should be mentioned that it was assumed that the units of "ppm" were the same in the solid as in the gas phase. The question of the solubility coefficient will be returned to at the end of this section.

The determination of the diffusion constant is equally straight forward, but an important assumption is necessary. As seen in Appendix A-9, the solution of time dependent problems in diffusion with reaction are difficult. Moreover, the actual curves of amount sorbed vs. time would have to be available for analysis, and these were not. Hence it was assumed that in these short times sorption takes place with a negligible amount of reaction, an assumption that appears to be justified by the data (15). Then the calculation of the range of diffusion constants consistent with the results is a standard problem (5). All that is necessary is the thickness of the sheet, which may be calculated from the basis weight (14). From such a calculation it was found that diffusion constants of 10^{-8} and 10^{-9} cm^2/sec were consistent with sorption in 24-48 hours, but 10^{-7} cm^2/sec was too fast and 10^{-10} cm^2 was too slow. Hence the values that were used in the illustrative calculations.

The calculation of the reaction rate constant, assuming a first order reaction, presents considerably greater problems. As seen in Appendix A-9, the full time dependent solution becomes quite difficult, so only the steady-state solution was used. This is given in Appendix A-11. This shows that at steady state, the slope, m, of the pollutant concentration vs. time curve is given by

$$m = \frac{C_s k}{\ell} \quad \frac{D}{k}^{1/2} \quad \tanh\left(\frac{k}{D}\right)^{1/2}\ell \qquad 20$$

where C_s is the surface concentration in the sheet. In this particular case, where the results indicate that diffusion is not the rate limiting step, C_s may be identified with the concentration after the first reversible sorption has taken place. Moreover, the values of m are known. They are given as follows (15), in parts/10^5/day: two rag papers with m=0.099 and 0.058; a group of nine papers of various types with an average m of 0.5; and a newsprint of 80% groundwood and 20% chemical wood with m=3.46. Then, knowing all the quantities save k, Eq. 20 may be solved for the latter by numerical iteration techniques. However, since all the values of C_s were not available for all cases, calculations were carried out for a range of values taken from the data for this quantity, as well as for the two values of D found to be consistent with the data as discussed above.

When the calculations were carried out, it was found that $kC_s/m=1$. It can be shown (18) that this indicates that the concentration of unreacted pollutant in the sheet is uniform, which is consistent with the reaction not being limited by diffusion, which in turn is consistent with the experimental results. The results are shown in Table 8. The two extreme values of k, 2.9×10^{-8} and 830×10^{-8} sec^{-1}, for the least reactive rag paper and for newsprint, respectively, are the two values used for illustrative calculations.

We now return to the question of S and to a fact that was mentioned above but was not discussed. This is the fact that the rate of the slow, fixation reaction was determined to be proportional to the square root of the concentration in the gas phase (15). The most reasonable explanation of this is that the concentration of unreacted SO_2 in the paper is also dependent on the square root of the concentration of SO_2 in the gas phase, i.e., the sorption isotherm is not linear, as we have assumed. These experiments were carried out at gas phase concentrations greater than 10 ppm, which is quite high--perhaps by a factor of over 100--for the concentration of pollutant found in air under normal conditions, a factor mentioned by the authors (15). It is not known if this square-root proportionality holds down to the usual air pollutant concentrations. If it does, the assumption that S is independent of the concentration, made for mathematical expediency, is not correct. However, it is felt that the qualitative nature of the results would not be changed, nor would the general conclusions.

2.10 Models Not Solved

There is a class of important models that we have not yet considered. These are models when the container holds tightly packed contents, so that diffusion into the contents as well as through the walls of the container is an important, rate limiting process. When we did consider the contents, they were either inert, or were loosely packed so that diffusion into them was not a rate limiting process. When this is not the case, the problem becomes one of two separate diffusion problems, but coupled through their boundary conditions. These are very difficult problems to treat analytically and are probably best handled experimentally.

2.11 Sealed, Impermeable Containers; Encapsulation

As has been seen from the analysis of the various models, and is obvious _a priori_, if record documents are placed in sealed containers impermeable to pollutant, then they are protected from the pollutant. The worst that can happen is that they react with the pollutant trapped in the atmosphere of the container or in solution in themselves at the time of sealing, and re-introduced when the documents are removed during normal usage. (This does not mean that the documents will not degrade, as will be discussed later in the report.) The question then naturally arises, "Why not store records in sealed, impermeable containers?"

There is, in fact, precedent for doing this with some types of records. Thus, ANSI standards PH 1.48-1982, "Practice for Storage of Black-and-White Photographic Paper Prints", and PH 1.43-1985, "Processed Safety Film Storage", both recommend sealed, impermeable containers ("enclosures" in the terminology of the standards) for the archival storage of the subject records. Archival storage conditions, defined for safety film, but presumably the same for paper prints, are, "...those that are suitable for the preservation of photographic film having permanent historical value." Why is this not recommended in cases other than safety film and photographic prints?

The answer is found in the standard for safety film itself. Sealed containers are _not_ recommended for cellulose nitrate based films, for these are inherently unstable and degrade and give acidic degradation products. In the case of paper, Dr. Charleton Bard (26), noted that photographic paper is pure alpha-cellulose, which is highly resistant to degradation and gives off no degradation products. With other, more degradable papers, sealing in a container may actually be worse than storing in the open, for the degradation products serve to increase the rate of degradation of themselves and perhaps other, less degradable, papers in the same container in an auto-catalytic manner. As will be discussed in a later section of the report, one of the principal reactions involved in the degradation of paper is hydrolysis. This reaction is catalyzed by acids, and since there are acidic degradation products, these further catalyze the degradation reaction. The harmful effect of a pollutant like SO_2 is not necessarily to react with the cellulose molecule but rather to be converted to SO_3 and hence sulfuric acid, which catalyzes the degradation. Paper at a normal regain contains approximately 4% water, which is an enormous reservoir of water available for hydrolysis.

Indeed, it was the opinion of all the experts consulted that, unless the paper is of high quality and resistant to degradation, sealing (or encapsulation) may actually be harmful, except, of course, for physical protection. Moreover, sealing good paper in a container along with bad paper may be harmful to the good paper. Also, the inclusion in the container of unstable substances like nitrocellulose also promotes the degradation of the other records.

While this is the feeling of the experts based on their long experience and is undoubtedly correct, direct laboratory evidence that sealing in containers is harmful is scanty. At this point it is helpful to define our terms a bit more precisely. By sealed containers we mean those that have no gaps as described in the section on the prototype container. By impermeable containers we mean sealed containers constructed of a material impermeable to the pollutant or other substance in question, i.e., where the solubility and/or the diffusion constant are zero. Such materials are aluminum, stainless steel, etc., and are specifically referenced in PH 1.48-82. By these definitions, encapsulation of a document between, e.g., polyester sheets, is not the same as placing it in an impermeable container, for the pollutant can diffuse through the sheets. Encapsulation is, indeed, the same as the model in Sec. 2.6, but without gaps, and, of course different dimensions and other parameters than the ones chosen for illustrative purposes.

We know of only two laboratory experiments that deal with the comparison of the degradation rate of paper in sealed or impermeable containers with the rate without containers but otherwise comparable conditions (27,28). The first of these was concerned with the degradation of Whatman papers in sealed glass tubes at 100C and a calculated Rh of 42% as compared to degradation at the same temperature and Rh an oven. It was found that the degradation rate, as measured by changes in reflectivity and the degree of polymerization, was greater in the closed tubes than in the oven. It should be noted, however, that this experiment does not necessarily mean that degradation was hastened by degradation products. The pressure -- particularly the oxygen pressure -- is greater in the tube than in the oven, and this could be the cause of the greater rate of degradation. The greater pressure is, in fact, the mechanism espoused by the authors.

The experiments by Shahani (28) are similar, but with distinct differences. Only the referenced letter and a personal conversation are available to us now; the work is still in progress. In this work, paper was encapsulated in polyester sheets, without holes and with holes to permit the escape of acidic degradation products, if any. The important results of this work are that for acidic or neutral papers, degradation inside the polyester envelope, with or without holes, is faster than it is without encapsulation. Most important is the effect of introducing paper with an alkaline reserve into the envelope. In the author's own words, "The acceleration in the decline of physical properties of acidic and neutral samples upon encapsulation can be eliminated by enclosing another sheet of paper containing an alkaline reserve in the same envelope." This very important result strongly indicates that whatever degradation accelerating substances are released by the degrading paper, they are probably acidic and perhaps are transmitted via the gas phase. What these substances actually are appears to be unknown.

2.12 Recesses

So far we have been concerned principally with containers. These, however, are not the only cases in which microenvironments may be established. There are numerous regions or spaces, e.g., an empty shelf, or the region over the tops of books packed on shelves (see figures on p.4 and p.17 in Ref.4) that have limited access to the ambient stack environment. These spaces, which we shall henceforth refer to as "recesses", provide for the possibility of a microenvironment, and, as with containers, we wish to determine how different this microenvironment is from the macroenvironment of the stacks proper.

In many--perhaps most--cases, these recesses can be considered to be a rectangular parallelipiped open on one side to the ambient stack atmosphere, and with the other five sides consisting of impermeable material. In cross section, then, the recess can be represented by Fig. 2, but _without_ the membrane barrier. Now, it is clear that the slowest mode by which the recess can exchange pollutant with the main stack atmosphere is diffusion. Any convection that may take place can only hasten the exchange. Hence we investigate diffusion into such a recess.

For this purpose, imagine such a rectangular recess with dimensions a,b, and c, in, respectively, the x,y, and z directions. One of the faces normal to the x direction is open; all other faces are made of impermeable material (e.g., steel shelving). We consider only the simplest situation. Other more complicated situations are easily handled, at least formally, but without adding any new insight. We imagine that the environment inside the recess is in equilibrium with the exterior environment, and, since the recess is open to the exterior, this means that the two environments are the same. We now make a sudden change in the pollutant concentration of the exterior environment and ask what happens to the concentration in the recess.

This is a standard problem in diffusion and heat flow. It is readily solved, and the solution will not be presented. Only the results will be given. What happens in this situation is that the change in concentration spreads into the recess, but the concentration in the spreading front is independent of the y and z coordinates. It is dependent only on the distance from the open edge of the recess, i.e., depends only on the x coordinate. What this means is that the rate at which pollutant spreads into the recess is _independent of the lateral dimensions of the recess_. Our task, then, is simply to choose a position in the recess and calculate the composition at that point as a function of time.

For purposes of illustration, a recess one meter deep was chosen and the composition at the end of the recess opposite the open end was calculated as a function of time. The diffusion coefficient, as in the previous calculations, was taken to be 0.2 cm^2/sec. The results for the ratio of the concentration to the exterior are as follows: after one hour, 0.018; after 12 hours, 0.85; and after 24 hours, 0.98. It is thus seen, that after 12 hours the environment inside the recess is essentially the same as the ambient environment. Any convection that may be present will hasten the attainment of equilibrium. Since 12 hours is a short time compared to the degradation processes of concern, we conclude that for all practical purposes the microenvironment in a recess of this depth will be essentially the same as the macroenvironment.

2.13 Conclusions

This concludes the portion of the report on models. There are several conclusions that can be drawn from the analysis and that are very likely independent of the assumptions made in it.

1) The microenvironment inside a container communicates with the macroenvironment outside it by diffusion through the walls of the container; by diffusion through any gaps or openings in those walls; or by pressure or temperature changes if there are gaps in the walls.

2) For an empty container with inert walls, the interior microenvironment eventually becomes the same as the macroenvironment if the latter is constant, or its average if it is fluctuating. If there are any gaps in the walls, the interior environment is always very nearly the same as the exterior environment, and follows any changes in the latter with only a small time delay. The time constant, or "relaxation time", for any changes in the microenvironment in the absence of gaps in the walls is given by $V\ell/ADS$, and hence depends on the design of the container through V, A, and ℓ, and on the materials of construction through D and S. If there are any gaps the expression for the relaxation time is the same but without S, and its value is very small compared to diffusion through the walls.

3) Presure and temperature cycles, for the ranges of change and time scales assumed for those changes, are about as effective as diffusion through walls in providing communication between the inside and outside of containers.

4) If the container holds reactive contents, i.e., the contents react with the pollutant(s) in question, then, in the absence of gaps in the walls, the microenvironment inside the container can be substantially different and more benign than the macroenvironment outside it. If gaps are present, then the microenvironment can be the same as the macroenvironment.

5) If the container walls can react with the pollutant(s) in its (their) passage through them, then essentially complete protection from the pollutant can be provided. This may even hold if there are gaps in the walls, provided the gaps are long and narrow.

6) The diffusion constant for the interface between sheets in a book is much lower than for diffusion in a gas, and may approach the diffusion constant in the solid phase.

7) Sealed, impermeable containers will obviously prevent any communication between the inside and outside of the container and hence provide complete protection from the exterior pollutants. However, if the contents are reactive, they may may give off degradation products that catalyze further degradation. (The contents "stew in their own juices"). The option of sealed, impermeable containers is limited to such items as

very high quality paper, safety film, and perhaps magnetic recording tapes.

8) Unless recesses are very deep, the microenvironment in them is essentially the same as the macroenvironment.

9) There is a very limited availability of data in the literature with which to make calculations from the models and to check them.

3. DEGRADATION AND ITS PREDICTION; DATA AVAILABILITY

3.1 Introduction

In this section we discuss the degradation of record materials and the prediction of permanence by laboratory tests--the so-called study of accelerated aging. These are very old and extensive subjects with an immense literature, and reviewing all of it would far exceed the scope of this project. Nor is such a full review necessary. In this report we are interested in degradation caused by air pollutants, and, even more specifically, how the microenvironment in containers may alleviate degradation. This considerably narrows the scope. Moreover, not all record materials need equal attention. Of the four principal record materials -- paper, photographic media, magnetic media, and optical disks -- the last two are not presently suitable for archival storage, perhaps as much for hardware reasons as for the inherent stability of the materials themselves (4). In comparison to paper, the ability to predict permanence, and the resulting standards for archival storage, are more advanced for other materials than for paper (4,29,30,31). Hence our main emphasis will be on paper.

Recalling that this report is concerned with laying out a program for the study of microenvironments and their consequences for protection from degradation, we shall also review the availability of data to permit the determination of microenvironments.

3.2 Paper Degradation

3.2.1 General Review

The degradation of paper is a subject that has been studied for a very long time indeed, and on which there is an extensive literature. Fortunately there are a number of recent reviews (32,33,34) which give references to other reviews as well as original literature. We obviously cannot write yet another review of paper degradation, and hence we will summarize the elements that are important for our purposes. These are,

1) There are a number of measures of degradation and the quantitative relationship between them is not always clear. These measures may be classified into two broad categories which may be called "chemical measures" and "physical measures". The chemical measures are those that deal with chemical changes that occur in the paper substance on degradation. These are (33): decrease in the degree of polymerization; increase in acidity; increase in carboxyl, aldehyde, ketone, and peroxide

content; changes in moisture regain; and changes in alkali solubility. The physical measures refer to changes in those physical properties that are of direct importance for the utility and use of the document. These are: decreases in fold endurance, tear strength, burst strength, and tensile strength; changes in elongation, modulus, tensile energy absorption, wet tensile strength, and changes in blue reflectance. To these should be added deterioration of image quality, but, of course, this is determined by degradation of the ink, not necessarily only the paper.

2) The single most important factor in determining the permanence of paper is its acidity. Papers with low Ph degrade seriously. Those with neutral or higher Ph (but not too high, for too high an alkalinity also leads to degradation) are relatively stable. For this reason, calcium or magnesium carbonates are added to papers to increase their stability. Standards for paper composition relating to their permanence are available (35,36).

3) The principal basic chemical reactions that occur in paper degradation are hydrolysis, oxidation, cross-linking, and thermal decomposition. Changes in bonding are listed here by Wilson and Parks (33), but this would not appear to be a basic reaction, but rather the result of one or more of them. Hydrolysis is the most important of these reactions, and since it is catalyzed by both acids and bases, the reason for keeping paper neutral or slightly basic is clear. Oxidation is catalyzed by transition metals (Fe,Cu,Mn).

4) Only a qualitative relationship between the basic reactions and either the chemical or physical measures of degradation is known. While it may be difficult, if not actually impossible, to relate the basic reactions quantitatively to the physical measures of degradation, it should be possible at least in principle to do this for the chemical measures.

5) As already mentioned above in Sec. 2.10, degradation products, presumably because they are acidic, catalyze the degradation of paper, leading to an autocatalytic degradation process unless these products are removed or neutralized. There is evidence that hemicelluloses are important contributors to this process (37).

The reason for re-stating these well-known facts is that we wish to put the action of pollutants into context. We now proceed to summarize what is known about the action of pollutants.

3.2.2 Sulfur Dioxide

The effect of sulfur dioxide on the degradation of paper and hence record documents has been studied for a very long time, and is the most studied of all the pollutants. An excellent account of early work is given by Kimberley and Scribner (38). Sulfur dioxide increases the rate of degradation of paper substantially, but it does not react with the cellulose molecule directly. Rather, it is converted to SO_3 (or sulfate) as already discussed in Sec.2.8, which increases the acidity of the paper and hence the rate of hydrolysis. In a readable, concise and prescient account of the requirements for enhanced degradation of library materials, Langwell (39) writes as follows:

> Analysis has brought to light some interesting facts which help in reaching an understanding of the mechanism of the reaction. In the first place books containing paper made before about 1750 may have the outer binding completely destroyed by atmospheric pollution and yet preserve the original strength of the paper almost unimpaired, since paper made before 1750 may contain very little metallic impurity. This suggests one process by which atmospheric sulphur dioxide can be changed to sulphuric acid in the paper, if it is assumed, as one has every reason to do, that the metallic impurity accelerates the conversion of sulphur dioxide to sulphuric acid. Laboratory experiments confirm this supposition, and show clearly that the presence of moisture is also necessary.
>
> A third factor which can be inferred from a consideration of the extreme dilution of the sulphur dioxide in normal air is the movement of the air; obviously sulphur dioxide cannot damage paper unless a sufficient amount of it can make contact with the paper. The essential factors are therefore; the amount of sulphur dioxide in the air; the amount of moisture in the air and the movement of the air. In the complete absence of any one of these factors paper cannot accumulate appreciable amounts of sulphuric acid, and would presumably last indefinitely. This is the modern theory of permanence.

He goes on to write;

> From these observations the remedies for impermanence should depend on:
> 1) Treating paper so as to remove the metallic impurity.
> 2) Treating the air to remove either the sulphur dioxide or <u>all</u> the moisture; the latter is neither practicable nor desirable.
> 3) Restricting the amount of air which is allowed to circulate round the books or paper.

That metals are important for the conversion of SO_2 to SO_3 (or sulfate) is borne out by the work of Hudson, et.al.(16), who found that the rate of "fixation" of SO_2 was increased by raising the copper or manganese content of the paper. Both these metals were more effective than iron. These workers also point out that sulfonation of lignin can also take place, which may account in part for the higher rate of fixation of SO_2 by papers containing groundwood.

That acidification and subsequent degradation by hydrolysis is the mechanism by which SO_2 degrades paper is borne out by studies by Hudson (40) of the surface acidity of pages in 25 old books. Copies of these books were obtained from two libraries: one located in a rural environment and one in the polluted atmosphere of Manchester, England. He found that the book pages were higher in acidity near the edges, and higher for the books stored in the urban than for those in the rural atmosphere. The more acid books showed more degradation. These data were subjected to a statistical analysis by Baer and Berman (41) with the following conclusions:

> ...to the degree that the variance in the contact pH for the two groups of books studied by Hudson can be attributed to library location and position on the page, the low pH at the edges of the page as compared to the center of the page may be attributed with great confidence to the differing conditions of storage for the two libraries. It should be noted that environmental factors in addition to the local SO_2 concentrations, e.g., average annual rainfall, frequency of use, maintenance practices, may have contributed to the observed differences.

From these and other studies (1,4,33) it may be concluded that the mechanism by which SO_2 degrades paper is by its conversion to SO_3 and hence sulfuric acid, and the subsequent acid catalyzed hydrolysis of the cellulose molecule and other components in the paper.

3.2.3 Oxides of Nitrogen

In contrast to the situation with SO_2, work on the degradation of paper by the oxides of nitrogen is very scarce. Certainly it is known that the cellulose molecule is oxidized by N_2O_4 to form primarily a carboxyl at the C-6 position and secondarily aldehyde and ketone groups at other positions in the molecule (42). Other polymers are known to undergo chain scission by NO_2 (43,44), but the only work that we have found that relates to the degradation of paper is a study of the degradation of cotton fabric (45). In this work, cotton fabric was exposed at room temperature and normal humidity to atmospheres separately containing various concentrations of NO_2 and HCl, up to 6% v/v. The results are somewhat puzzling. Thus, HCl causes greater degradation in tensile strength than does NO_2, but both show the same changes in fluidity in cuprammonium solution, and hence presumably comparable changes in degree of polymerization. Moreover, NO_2 causes large changes in carboxyl content, while HCl causes none, and larger changes in copper number than does HCl. These results imply that NO_2 causes about the same amount of hydrolysis (decrease in the degree of polymerization) as does HCl, plus some oxidation that HCl does not produce , yet does not degrade tensile strength as much. This puzzling result, along with the paucity of other work shows that this area is greatly in need of work if the effect of NO_x on paper is to be understood.

3.2.4 Ozone and Other Pollutants

Ozone concentrations in the National Archives Building, at least in winter, are at undetectably low levels (2). Their summer levels are unknown, but data from libraries and museums in other places imply that they might be high (4,p.20). What the level is inside containers is also unknown, but one can hypothesize that it would be low, even for containers with gaps (provided they are long and narrow), for such a reactive molecule would have trouble getting into a container without reacting with the walls.

Whatever the case, the action of ozone on paper is very little studied. Bogarty, et.al. (46) showed that ozone in concentrations found in polluted air (<0.06 ppm) degraded cotton when wet but not when dry, although the exposures were only of thirty days duration--hardly archival times. These studies appear to be borne out by those of Morris (4,p.18). There is clearly a paucity of data on the effect of ozone on paper.

There are a number of air pollutants found in outdoor air that are potentially detrimental to paper (and other record materials) (4, p.13), and still more found in the indoor air of libraries and museums (1). Among the latter are formaldehyde, organic acids, and oxides of nitrogen, the last given off by materials containing cellulose nitrate, such as book bindings containing pyroxylin. With the slight exception of NO_2, none of these has been studied, although since many of them are acidic, the presumption is that they are harmful.

3.3 Leather

Somewhat out of place we discuss leather. This is a special case. Many books in the Archives are bound in leather, and they are not in containers. Some of the bindings show signs of severe degradation. However, the degradation of the bindings does not necessarily mean a similar degradation of the pages inside the book, although this might be hastened by the lack of a container. If the bindings do not have an intrinsic value, the book can always be re-bound, which, however, is an added expense.

As with paper, the main degradation caused by air pollutants is via the acidity caused by SO_2, which is added to the normal acidity resulting from the processing (1,34). With respect to other pollutants, there is the same paucity of data as for paper. It is possible that the degradation of leather may lead to the formation of volatile acids and hence an increase in their concentration in the ambient stack environment, a variant of the situation in impermeable containers discussed in Sec. 2.10. There appear to be no data on this effect, if indeed it exists.

3.4 Lifetime Prediction; Accelerated Aging

3.4.1 General

One of the principal goals of materials science and engineering has always been the prediction by laboratory tests of the lifetime in service of materials and structures. The ability to predict the life of an object before that object is put into service can lead to the use of proper materials and design and hence prevent unanticipated failures with a consequent saving of human and capital resources, the preservation of objects of social and cultural value, and, often, the saving of human life. Thus it is hardly surprising that the study of the laboratory prediction of lifetime in service of record materials has been a long and continuing effort. Here we discuss paper.

An excellent review of these efforts is given by Roberson (47), who also lists other reviews, and there are a number of other papers (37,48-55) that bear on important aspects of the subject. As before, we cannot review all this work, and will only discuss those features that are important for our purposes.

Briefly, then, in these studies advantage is taken of the fact that temperature increases the rate of chemical reactions. A measure of degradation

is chosen and measured as a function of time of exposure of a sample to a temperature that is high enough that the work can be carried out in a reasonable time. This gives the rate of degradation according to that measure as function of temperature. This is not always simple to do because plots of the measure against time are not always linear (51,53), but this can sometimes be remedied by different handling of the data (52) or by other semi-empirical methods (53). Whatever is done, a rate constant is determined at different temperatures. An Arrhenius plot of all these is made. This is used to extrapolate to room temperature, and hence a degradation rate at room temperature is obtained. The most common measures used are one or more of the physical measures discussed in Sec.3.2.1, most commonly fold endurance and blue reflectance. In special cases when the data are available, the results of accelerated tests may be compared and correlated with many years of natural aging (49,40). With some measures and with some papers, good correlation exists (49), and then accelerated aging can become lifetime prediction.
Then a statement like, "Forty eight hours at 100C is equivalent to 13 years of natural aging" can be made, but the correlation is totally empirical, and does not necessarily hold out of the context in which it was derived. Nevertheless, two useful standards (56,57) to give a relative estimate of permanence have been developed on this basis. These involve heating papers for 72 hours at 105C, and the fold endurance measured. With the proviso that "It has not been established that this test method is suitable for papers with a high groundwood content, and no evidence is available of its being satisfactory for coated paper or for those containing wet-strength resins", the ASTM standard goes on to state,

> The heating condition specified in this test method produces the deteriorative reactions, excepting photochemical, of the normal components of papers similar to those occurring on long aging of paper in air at room temperature. It is recognized that heating paper under the conditions specified is not a normal treatment which the paper would receive in use, but research has indicated that the results of heating under the prescribed conditions correlate with those of normal aging. The effect as measured by this method is approximately equivalent to that of normal aging for 25 to 28 years.

While this approach can give a relative ranking of papers, it is recognized that there are deficiencies in it (47,53,54,55). First, for it to be useful, the Arrhenius plots for various papers must be linear and <u>parallel</u>, otherwise individual plots would have to be made for each paper (53). Second, and perhaps most important, it is almost axiomatic in lifetime prediction that the basic reactions that affect degradation <u>and their relationship to the measure of degradation</u> must be known if accurate accelerated tests are to be developed. In the particular case of paper, as discussed in Sec. 3.2.1, permanence is usually defined on the basis of one or more of the physical measures, whereas the basic reactions are hydrolysis, oxidation, cross-linking, bonding, thermal decomposition and perhaps others. The relationship of these to the physical measures are not known in any detail. Thus, Browning (58) writes,

> The changes in a paper property with time are not determined by any

> single chemical reaction whose effects can be isolated and controlled. Hence, applications of conventional kinetic treatment to aging data on paper are largely empirical.

Third, there are the conditions of accelerated aging. In natural aging, the paper is at customary relative humidity and hence contains several percent water. However, when heated in an oven at 105C, as is done in the standard test methods, the paper is desiccated. Indeed, the standards require that the paper be desiccated before testing so as to approach its final condition from below. It is well established that moisture content increases the rate of degradation (54,55), whether achieved by enclosing samples in sealed tubes or placing them in a humidity controlled high- temperature chamber, which is more difficult experimentally. It would seem natural to use conditions such that the moisture content under the test conditions are the same as in natural aging, including cycling of temperature and humidity. Roberson writes (47):

> Since the purpose of accelerated aging is to duplicate natural aging chemically and physically, the degree to which this is accomplished is the proper measure of a test method's validity. It seems logical that moist aging with cycling of temperature and humidity might do this better than dry-oven aging, but it has not yet been demonstrated.

By the final comment he apparently means that no empirical correlation between moist aging and natural aging has been made.

In this context we return to the subject of aging in sealed tubes. Such studies were carried by Browning and Wink (53) as a substitute for the experimentally more complicated moist high-temperature oven conditions. The rate of degradation in these sealed tubes was about eleven times as fast as in dry aging. Also, apparently reporting from work not available to us, Roberson reports that degradation in sealed tubes occurred at the same rate as in moist oven aging. This contrasts with the results of Santucci and Zappala-Plossi (27) who found aging in tubes to be more rapid, a result that seems to us and to Roberson to be more reasonable for the reasons discussed in Sec. 2.10.

Finally we should discuss cycling. In normal usage, both temperature and humidity will not usually be constant, although they practically are in the National Archives storage conditions. If the measure of degradation really follows the Arrhenius equation, and the time-temperature variations are known, then the effect of temperature is easily calculated by using an appropriately weighted mean temperature. However, if relative humidity also changes, with the consequent hysteresis effects this causes, then the problem becomes more difficult. This problem of temperature cycling and humidity was investigated by Cardwell (59) who reported that cycling between 105C, dry, and 23C, 50% Rh, caused greater degradation than constant aging at 105C. His description of the experiment is, however, not completely clear, and this merits further investigation.

To summarize, accelerated aging to give a relative measure of permanence is both possible and useful. To make accelerated aging a more quantitative predictive technique, relationships between the physical measures of aging and the basic primary chemical changes that occur on aging need to be established. Then with a knowledge of the activation energies of the basic chemical reactions, there is at least a hope of putting accelerated aging on a fundamental, quantitative basis. Doing this is likely to be a long and difficult task, but without it prediction of lifetime by accelerated aging will remain a useful but empirical science.

3.4.2 Accelerated Aging and Pollutants

So far we have not said anything about pollutants. The reason for this is simple; there is very little in the literature on accelerated testing for the effect of pollutants. In work with SO_2, Kimberly (60) exposed several papers to an atmosphere containing 1-9 ppm of SO_2 for 240 hours at 30C and 65% relative humidity. Fold endurance decreased considerably, acidity and copper number increased (indicating hydrolysis), but tensile strength did not change. Since the concentration of SO_2 used was substantially higher than that found in normal usage, this can be considered an accelerated test. In a similar vein, Edwards, et.al., (15), using their rates for SO_2 sorption and conversion to SO_3, as discussed in Sec. 2.8., were able to extrapolate their rates to a concentration of 0.1 ppm SO_2, which is approximately the concentration in polluted atmospheres. From this they calculated that in 25 years book papers would pick up about 0.7% SO_3. This agrees remarkably well with results by Langwell (61) on actual books. Since the Edwards experiments were carried out at higher concentrations (>10 ppm) and were for relatively short times, these again can be considered accelerated aging experiments, although no measure of degradation was determined. The acceleration results from an increase in the SO_2 concentration in the atmosphere, resulting in a higher sulfate content and hence acidity and hence hydrolysis and degradation of the paper. How far this can be carried is not known.

The work of Schreiber, et. al., (45) on the degradation of cotton by NO_2 has already been discussed. Since the concentration of NO_2 used was 6%, this was clearly accelerated aging. Similarly, the work by Jellinek, et.al., (43,44,62)on chain scission in nylon and chain scission and nitration in polystyrene by NO_2 using quite high pressures (0.05 to 60 cm Hg) might also be considered accelerated aging, although it was not done for this purpose. Both Hudson, et.al, and Jellinek, et.al., carried out experiments at various temperatures and were able to obtain activation energies. Another group of workers (63) were actually concerned with accelerated aging of nylon and Kevlar by smog and ozone, using tensile strength as the physical measure of degradation. It was found that smog seriously degraded the tensile strength, but ozone did not. The latter result is in sharp contrast with the results of Jellinek and Chaudhuri (62) who, however, used degree of polymerization as the measure of degradation. Finally, in two papers, Igarashi and DeVries (64,65) investigated the effect of O_3, NO_x, SO_2, and u.v. radiation on nylon and polyethylene, using tensile strength as the measure. When samples were exposed under stress, the environmental factors increased degradation, but without stress there was little or no increase.

These few papers, on materials which are of only marginal interest for record materials, illustrate the state of knowledge about the effect of environmental factors on the rate of degradation of record and container construction materials. Clearly, a great deal of work needs to be done in this field if accelerated aging by pollutants is to be understood and become a useful discipline.

3.5 Data Availability

In this final section of this part of the report, we examine the availability of data. The data in question are data for diffusion constant, solubility coefficient, and, what is more readily available because of its ease of measurement, their product, or permeability, P. We shall also be concerned with the reaction rate constant, k, as discussed above, as well as the reaction involved. We limit ourselves to the action of pollutants.

Literature searches using the Chemical Abstracts data bases were conducted. For SO_2, presumably because of the interest in permeation tubes, there were relatively speaking quite a few publications, but not many of them were concerned with materials of interest to us. For other pollutants there were relatively few publications.

An excellent compilation of data on transport properties for SO_2 in various materials is that of Felder, et.al., (66). While this compilation is for many polymers, the data for those likely to be of interest in this study are given in Table 9. While this may seem like a lot of data, it should be noted that they come from only five references. It should also be noted that the units of S are different from those defined in Appendix A-1. To obtain those, the values in Table 9 should be multiplied by 76. The wide variation of results (note particularly those for polyethylene) from different laboratories should be noted. There is only one result (of questionable validity) for paper, and that only for the permeation coefficient. This was the main reason for going through the analysis carried out in Sec. 2.9. It seems rather clear that when experimental investigations are carried out, transport coefficients will have to be measured on the actual materials being investigated.

No data on the reaction rate constant for SO_2 were found other than those discussed in Sec. 2.9.

For NO_2 there only three papers that give results (43,44.62). The first of these is for polystyrene, and the values are: $D=2.5x10^{-9}$; $S=0.4$ $cm^3(STP)/cm^3.cmHg$. Two rate constants can be determined, one for chain scission and one for substitution on the tertiary carbon on the main chain. These are, respectively, $2.4x10^{-8}$ sec^{-1} and approximately $1x10^{-5}$ sec^{-1} at room temperature. Rate constants for chain scission in nylon 66 for NO_2 and O_3 are also available (44,62). Again, if experimental investigations are carried out, transport coefficients and reaction rate constants will have to be determined.

3.6 Conclusions

Finally we list a number of conclusions that can be derived from the information presented in this section.

1. Degradation can be characterized by a number of chemical and physical measurements. The chemical measures are closer to the basic chemical

reactions that occur on degradation, but the physical measures are more closely related to the actual utility of record documents.

2. The relationship of the physical measures of degradation to the basic chemical reactions that occur in degradation are known in only a qualitative way. To put accelerated aging on a firm basis, this relationship should be determined insofar as possible. This is likely to be a long and continuing task.

3. The degradation products of paper and other record materials are known or suspected to increase the rate of degradation, and hence to cause degradation to be autocatalytic. What these degradation products are is not known. It is suspected that in the case of paper they are acidic and promote further degradation by hydrolysis. It is not known if they are gaseous and hence capable of transmission through the gas phase..

4. Sulfur dioxide in paper acts by conversion to SO_3, and thence to sulfuric acid. The rate of this reaction is increased by heavy metal ions. This increased acidity causes an increase in the rate of hydrolysis and hence degradation of the paper. Its action on other record or container wall construction materials is not known. It may be inert in some of them.

5. The reactions of NO_2 with cellulose are rather well known, but their relationship to the physical measures of degradation in paper are not. Data on transport properties are not known to us.

6. The action of ozone on records has not been studied. It is known to degrade cotton fabrics under certain circumstances, and to react with cellulose, but its effect on the physical measures of degradation is not well known.

7. The accelerated aging of paper without consideration of the action of pollutants has been a study of long duration, and has resulted in two useful standards. Two important questions remain: the effect of humidity, and the effect of degradation products, which is clearly of central importance if degradation in sealed containers is to be predicted.

8. There are only a few experiments directed at the accelerated aging of paper in the presence of pollutants, and none on other materials of interest as either record or container wall materials. As a simple example of the type of experiment that has not been done, consider the following. The rate of reaction of a pollutant can be increased by raising the concentration or by raising the temperature. However, raising the temperature decreases the solubility, which decreases the rate of reaction. Thus, the relative effects of temperature and solubility have not been sorted out.

9. The availability of data on transport properties and reaction rate constants is such that these will have to be determined on the actual materials under investigation when experimental investigations are carried out.

4. A RESEARCH PROGRAM

4.1 Introduction

It is clear from the structure of this report, and is evident ab initio, that the problems of concern in this whole question of microenvironments fall into two areas:

1. What are the microenvironments experienced by record documents?, and

2. Given an environment, micro or macro, how rapidly do documents degrade?

The aspects of the environment that are of concern are temperature, relative humidity, pollutant concentration, and the important question of the presence, nature, and action of degradation products. The principal emphasis here is on pollutants and degradation products. Logically, then, the research should address these two areas. This follows the structure of the report, and since conclusions were given at the end of the two main sections of the report, it is necessary to develop a research program that answers the questions posed in those summaries. Here we describe such a program.

4.2 Microenvironments

In this section of the report a number on models that relate the microenvironment inside a container to the macroenvironment (and any changes in it) outside it were developed. If (a significant "if") these models were known to be correct, then a knowledge of the container dimensions, and the relevant parameters D, S, and k for the various pollutant/container wall combinations would permit the calculation of the microenvironment inside the container. But, as detailed in Sec. 2, a number of approximations had to be made in the development of the models, so their validity has to be checked. Hence an experimental program, supported by theoretical analysis, to check out the models should be considered. While this program might be called, "validation of the models", it should be noted that a great deal of important information on microenvironments will be developed, whatever its intent. Specifically the following experimental investigations are suggested. This largely follows the analysis in the previous text.

4.2.1 The Container with Inert Walls

This is the simplest of the investigations. While it is probably not applicable to the paperboard container used as a prototype in the report for illustrative purposes, since its walls are probably reactive, it is likely applicable in other cases where the wall materials are inert. This, in turn, is likely to occur only with SO_2, since, as was seen, NO_2 and O_3 are quite reactive. The objective of the investigation is to determine, in this simplest case, how the microenvironment inside the container is affected by changes in the exterior macroenvironment. As far as is experimentally possible, actual containers should be used. The effect of gaps should be studied, for, as was seen in the development, they are likely to be very important, and the "breathing" as well as the diffusion modes should be investigated. Experiments with the container empty and filled with reactive documents should be carried out.

As part of this investigation the coefficients D,S and k will have be determined for the actual pollutants, wall materials and record materials involved, for otherwise a purely empirical investigation with hardly any opportunity for significant analysis will result. The important point to note is that if the models are verified, or an applicable model is developed, then it is only necessary to measure these coefficients to predict what would occur in a new and untested situation.

It is possible to do at least a part of this investigation (e.g., the empty container) without using a pollutant gas. This is strongly discouraged. Even though it would then be possible to predict what would happen with a pollutant, assuming an applicable model is developed, it would probably not be wise to proceed without actual experiments with pollutants. Moreover, it is unnecessary to use non-pollutant materials. Sulfur dioxide with a convenient radioactive isotope for analytical purposes would appear to be a natural candidate as a pollutant gas.

4.2.2 The Container with Reactive Walls.

This is viewed as perhaps the most important investigation that can be carried out. As noted in Sec. 2.7, if the pollutant cannot get through the container walls, then the contents are obviously protected from them. The only question that then arises is the effect of degradation products.

An experimental program that investigates this question would go as follows. First, determine the diffusion and solubility coefficients, and the reaction rate constant for one of the wall material/pollutant combinations. In this case, paperboard with and without $CaCO_3$, and with and without lignin would seem to be very appropriate, as would SO_2 because of the ease of measurement and because some measurements already exist in the literature (13-15). Then experiments with an actual container to determine the interior microenvironment as a function of the exterior macroenvironment could be carried out. In this case the prototype container, or a similar one, would appear to be highly appropriate. Experiments with and without contents should be carried out. The effect of gaps should be investigated, especially the effect of their aspect ratio, for as pointed out in the text, long narrow gaps might prevent the entrance of pollutants if the wall material is sufficiently reactive.

A full analysis of the experimental results derived from these investigations would very likely require a full solution of the time dependent diffusion problem. (Recall that only the steady state case was used in this report.) This solution was sketched out in Appendix A-9. To apply it would require more theoretical work. This would be desirable but not completely essential. A great deal of progress could be made experimentally with good experimental design and analysis.

This is deemed to be possibly one of the most rewarding of the investigations that could be carried out.

4.2.3 Degradation Products; Encapsulation

It follows from the discussion in Sec. 2.11 and Sec. 3.4 that if degradation products are not given off, or they do not catalyze further degradation, sealing documents in impermeable containers protects them from an aggressive environment. If degradation products are given off and do promote further degradation, then sealing documents in an impermeable container will still protect them from exterior pollutants but might compound the degradation problem by promoting degradation by the degradation products because these are now prevented from diffusing away from the documents. However, if these products can be removed from the container by the wall material, either by reaction with them , or because the products can diffuse through the walls, the container will at least not worsen the situation. Note that neither of these two kinds of container can prevent the degradation of inherently degradable materials; the best they can do is not to aggravate the situation. There is no substitute for high quality record materials. The first case, in which the products can react with the container walls, might apply to the $CaCO_3$ filled paperboard container, while the second might apply to a polyethylene shrink-wrapped book, although in this case the shrink-wrap might not protect the book from exterior pollutants. This latter situation is in fact a special case of the situation in Sec. 4.2.1, except that here we are now concerned with diffusion out of degradation products, and diffusion in of pollutants.

It is the opinion here that not much can be done on this problem until the degradation products are identified. Are they organic acids, aldehydes, ketones, nitrogen oxides, or what? Are they gaseous or not, and even if not, do they exist in the vapor phase? How are they transferred from one document to another? By diffusion on contact or by transfer via the gas phase?

It is felt that until these questions are answered, only empirical progress can be made. While this could prove useful (see Ref. 28), it is felt that modern analytical techniques like gas chromatography-mass spectrometry provide an opportunity for the identification of these products. An experimental program on their identification would appear to be very much in order and would begin to answer the vexing questions about the nature and likely effect of these products.

When considering an experimental program, it should be remembered that the primary, and perhaps sole, interest here is on degradation products in the gas phase, for only then is the microenvironment changed. Then the effect of containers becomes relevant. It is interesting and important to know, for example, that the C-6 carbon on cellulose is oxidized to a carboxyl on degradation, but not relevant to the problem of microenvironments. Only if that carboxyl is subsequently released as, say, formic acid does it affect the microenvironment in the container and hence influence another piece of paper remote from the one in which it originated. An experimental program of this type should include paper of various types as well as leather, pyroxylin containing book bindings, and other materials of interest. An obvious follow-up study is the reaction of these products with wall materials and their diffusion through them.

4.2.4 The Book Problem; Folders

The problem of the mechanism of entry of pollutants into book sheets was discussed in Sec. 2.8. There, on the basis of a simple calculation, it was concluded that the interface between sheets in a book is probably of a complex nature with a diffusion constant that is much lower than for gases, but whose magnitude is hard to estimate. Aside from a more thorough theoretical investigation, no particular course of action suggests itself. Moreover, it is not clear that an investigation of this problem would be very useful. It seems quite clear that the more tightly books and documents in folders are packed, the more the center portions of the sheets would be protected. Their edges, in the absence of a container, will always be exposed to the macroenvironment, however tightly packed, and in a container, the problem becomes one of those already discussed. As a result, no particular research program is suggested.

4.3 Degradation; Lifetime Prediction

4.3.1 Introduction

The studies described in the previous section can be relatively short-term, since they have the well defined goal of validating and/or developing microenvironment models, or, as in Sec. 4.2.3, of identifying degradation products. When it comes to the problems of concern in this section, the research tends to be longer range, with goals that, while capable of definition, are not as easily capable of attainment. The problems can be grouped into three categories: the relation of basic chemical degradation reactions to physical measures of degradation; the chemical effect of pollutants on record materials; and accelerated aging by pollutants. We will take up each of these in turn.

4.3.2 Relation of Basic Reactions to Physical Measures of Degradation

As discussed above in Sec 3.2, this is an important area of research since a knowledge of these relationships is necessary to put accelerated aging on a sound fundamental quantitative basis. A research program in this area would include the identification of the basic reactions involved, and the measurement of their rates and activation energies. While difficult, this is the easy part. The difficult part is relating these to the physical measures. While, for example, a great deal of work has been done on the relationship between tensile strength and degree of polymerization (73), a chemical measure of degradation which can be in turn related to hydrolysis, very little has been done on the relationship for the more commonly used measure of fold endurance. This whole area merits attention, but it should be considered a long-range continuing study rather than one with a specific end, except possibly in specific cases.

It should be pointed out, however, that if research on the identification of degradation products as in Sec. 4.2.3 is undertaken, it could be considered part of this study as well, for it would go a long way toward identifying the basic reactions and their mechanism.

4.3.3 Chemical Effects of Pollutants on Record Materials.

This study involves the reactions that occur between pollutants and record materials as well as their rates and mechanisms. Again, this is important for the prediction of lifetime in the presence of pollutants and for the development of accelerated aging procedures.

It will be noted, however, that a part of this information will have been developed if the research programs described in Secs. 4.2.1 and 4.2.2 are pursued, for carrying out those programs involves the reaction rate constant of pollutant with both wall and record materials. The present study could be considered an extension of that work to more pollutant/material combinations, and carried out in more depth.

4.3.4 Accelerated Aging by Pollutants.

As was seen in Sec. 3.4.2, very little work has been carried out on accelerated aging in the presence of pollutants, yet it is an important area if the effect of pollutants is to be known in a quantitative manner. As in the development of all accelerated tests, the mechanisms and activation energies of the various reactions should be determined, as well as, ideally, their relationship to the physical measures of degradation. Some of this information would have been developed if the work carried in the previous section and in Secs. 4.2.1 and 4.2.2 is carried out. Nevertheless, to carry out such a program properly will be a long effort, albeit a worthwhile one. However, it is also possible to proceed more empirically. Thus, having chosen a record material-pollutant combination, the effects of concentration, temperature and humidity could be investigated. The problem here would be in the relationship of the results of such an investigation to performance in service. There really is no way to do this without a comparison of the experimental results to service results as was done for paper (49,50). However, such an empirical study could permit the <u>relative</u> ranking of pollutant/material combinations. The whole question of sealed tube aging naturally arises in this study, for moisture will have a profound effect, and such aging again brings up the question of degradation products.

4.4 Summary and Conclusions.

The research program laid out can be grouped into seven elements, which may be listed as follows.

1. Microenvironment and reaction in a container with inert walls.

2. Microenvironment and reaction in a container with reactive walls.

3. Identification of degradation products.

4. The "Book Problem" and folders.

5. Relation of basic degradation reactions to physical measures of degradation.

6. Chemical effects of pollutants on record materials.

7. Accelerated aging with pollutants.

This program would, in our view, go a long way toward carrying out the recommendations of the NAS Committee (4), and go beyond them in developing the effect of pollutants on lifetime in service. Setting priorities among the elements of such a program requires a set of criteria, and many different orderings can be achieved depending on those criteria. Using the criteria of relevance to the problem of microenvironments in containers and the probability of achieving significant results we would place the elements of the program in the following order: 2,1,3,7,6,5.

Element 4 is omitted for the reasons given in the previous section. Element 6 is low on the list because a lot of the information that would be developed in this element would be developed in carrying out elements 1 and 2. Element 5 is low on the list despite its importance because it should really be considered to be a continuing background research effort and probably would have only long-term impact. Elements 1 and 2 are obviously central to the problem of containers and their utility, and element 3 is central to the problem of sealed, impermeable containers. Element 7 is placed where it is because of the importance of predicting performance in service in the presence of pollutants. Finally, it should be realized that this is a subjective listing based upon one set of criteria. Other criteria would very likely lead to another ordering. Indeed, depending on resource availability and priorities, some elements can be omitted entirely.

Acknowledgements

The author is pleased to acknowledge gracious, courteous and uniformly helpful discussions with Professor Norbert Baer, Professor Glen Cass, Mr. Peter Waters, Dr. Charleton Bard, Dr. Chandru Shahani, Mr. W.K. Wilson, Dr. Leslie Smith, and Dr. Alan Calmes and the rest of the NARA staff.

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TABLE 1

Dimensions of Prototypical Container

	Volume, cm^3	Area, cm^2
Empty Box	11960	3070
Full Box	2700	1420

Thickness of Wall	0.18 cm

Gap

Area	7.62 cm
Diffusion Length	3.28 cm

TABLE 2

Relaxation Times for Diffusion Into a Box With Unreactive Contents

Values are in seconds

D are in cm^2/sec

	$D=10^{-8}$	$D=10^{-9}$	Gaps $D=0.2$
Empty Box	2.34×10^6	2.34×10^7	2.50×10^4
Full Box	1.14×10^6	1.14×10^7	5.63×10^3

TABLE 3

Values of $1+\omega^2\tau^2$ for Box Filled With Inert Contents

	Difusion Through Walls		Diffusion Through Gaps
	D=10^{-8}	D=10^{-9}	D=0.2
Empty Box	202	$2.01\text{x}10^{4}$	1.02
Full Box	48.7	$4.77\text{x}10^{3}$	1.00

TABLE 4

Parameters for Box Filled With Reactive Documents

	Diffusion Through Walls	Diffusion Through Gaps
Unoccupied Volume, cm^3	7330	7330
Volume of Contents, cm^3	4630	4630
Area, cm^2	3070	7.62
Diffusion Length, cm	0.18	3.18
Diffusion Constant, cm2/sec	10^{-8}	0.2
S	30	30
k, sec^{-1}	$2.9x10^{-8}$; $830x10^{-8}$	$2.9x10^{-8}$; $830x10^{-8}$
τ_1, sec	$2.85x10^7$	$1x10^4$
τ_2, sec	$3.63x10^7$; $1.26x10^5$	3.63x107; $1.26x10^5$
τ_1/τ_2	0.79; 225	$2.8x10^{-4}$; 0.08

TABLE 5

Concentration Ratios for Zero Flow Into Container With Reactive Walls

kx108 sec^{-1}	Dx10^8 cm^2/sec	C_1/C_2
11.6	1	0.84
2.9	1	0.96
11.6	0.1	0.28
2.9	0.1	0.663
115	1	0.28
29	1	0.663
115	0.1	0.0045
29	0.1	0.09
830	1	0.011
210	1	0.15
830	0.1	$1.5x10^{-7}$
210	0.1	$5x10^{-4}$

TABLE 6

Concentration Ratios in Container With Reactive Walls Half Filled With Reactive Contents

$Dx10^8$ cm^2/sec	$k_c x10^8$ sec^{-1}	$k_w x10^8$ sec^{-1}	C_1/C_2
0.1	2.9	2.9	0.094
0.1	2.9	830	$1x10^{-7}$
0.1	830	2.9	$3.8x10^{-4}$
0.1	830	830	$1x10^{-9}$
1	2.9	2.9	0.54
1	2.9	830	$9.1x10^{-3}$
1	830	2.9	$4.4x10^{-3}$
1	830	830	$2.4x10^{-4}$

TABLE 7

Diffusion Into Book After One Day

Distance from Edge of Book, cm	C_1/C_2 Between Sheets	C_1/C_2 Center of Sheet
1	0.96	0.87
2	0.92	0.83
3	0.88	0.80
4	0.84	0.76
5	0.80	0.73
10	0.65	0.59

TABLE 8

Calculation of Reaction Rate Constant From Data of Hudson

C_s $\times 10^5$	m $sec^{-1} \times 10^{10}$	k $sec^{-1} \times 10^{8}$	kC_s/m
5	0.058	11.6	1.00
10	0.058	5.7	0.98
20	0.058	2.9	1.00
5	0.58	115	0.99
10	0.58	58	1.00
20	0.58	29	1.00
5	4.1	830	1.01
10	4.1	410	1.01
20	4.1	209	1.02

TABLE 9

Transport Coefficients for SO_2 In Various Materials

Material	T,C	$Px10^{10a}$	$Dx10^{9b}$	S^c	Reference
Polyethylene (Visqueen)	6.5-42	9.0-7.0			67
	25	2.09^e	112	0.0191	13
	25	6.2^f	85.4		
	25	84.0	180	0.47	70
(Polyane)	22	43.4	3.0	1.45	68
(NSR-CSSR)	25	$21.8-31.6^d$	...	...	69
Polypropylene (Maurylene)	22	6.18	0.35	1.71	68
Polycarbonate^f	25	17.5	0.63	2.96	13
Polyamide (Nylon 11)	25	1.18^f	0.32^f	1.23^f	13
(Rilsan)	22	21.1	1.0	1.84	68
Polyethylene-terephthlate (Mylar)	22	5.27	0.16	3.29	68
Cellulose Films	22	52.7	2.7	1.98	68
Regenerated Cellulose, dry	24.5	0.00172			71
100% Rh	24.5	37.9			69
Paper	25	1.31-6.74			69
Nitrocellulose	25	176	0.79	0.22	72

a) $cm^3(STP).cm/sec.cm^2.cmHg$
b) cm^2/sec
c) $cm^3(STP)/cm^3.cmHg$
d) See note on Ref.69
e) SO_2 partial pressure >25cm Hg.
f) For partial pressure of SO_2 approaching zero.

FIGURE CAPTIONS

1. Drawing of the box used as the prototypical container.

2. One dimensional representation of diffusion into a container.

3. Ratio of the interior and exterior concentrations as a function of time for the empty box or a box filled with inert contents. F=Full; E=Empty. The numbers alongside the curves are the values of the diffusion constant.

4. Assumed exterior variation of pollutant concentration.

5. Assumed pressure or temperature variation. The variation need not be linear between low and high values.

6. Ratio of the interior and exterior concentrations as a function of time for pressure and temperature cycling.

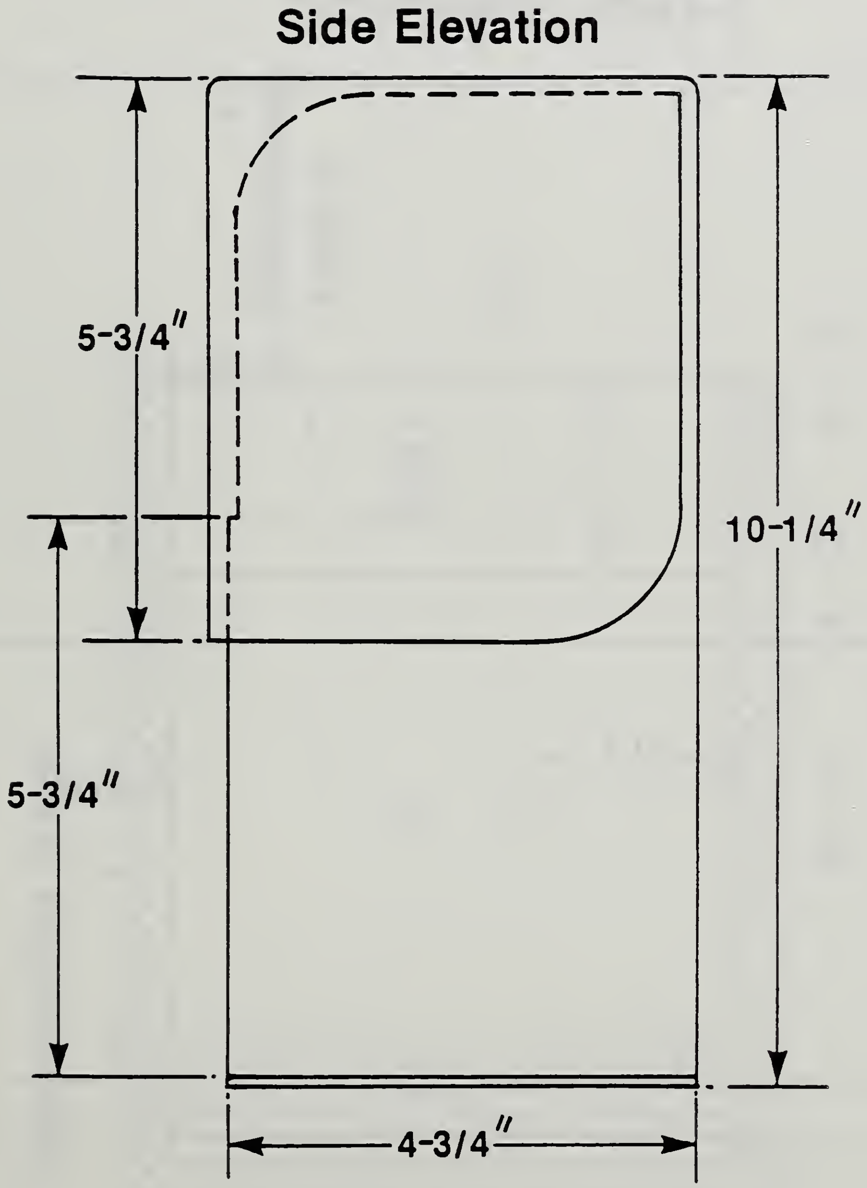
7. Ratio of the interior and exterior concentrations as a function of time for the box holding reactive documents. The numbers beside the curves are the reaction rate constant and the diffusion constant for the wall material.

8. Same as Fig.7 but diffusion is through gaps.

9. Concentration of reacted pollutant in box contents as a function of time for diffusion through unreactive walls for two values of the reaction rate constant. The straight lines are in the absence of a container.

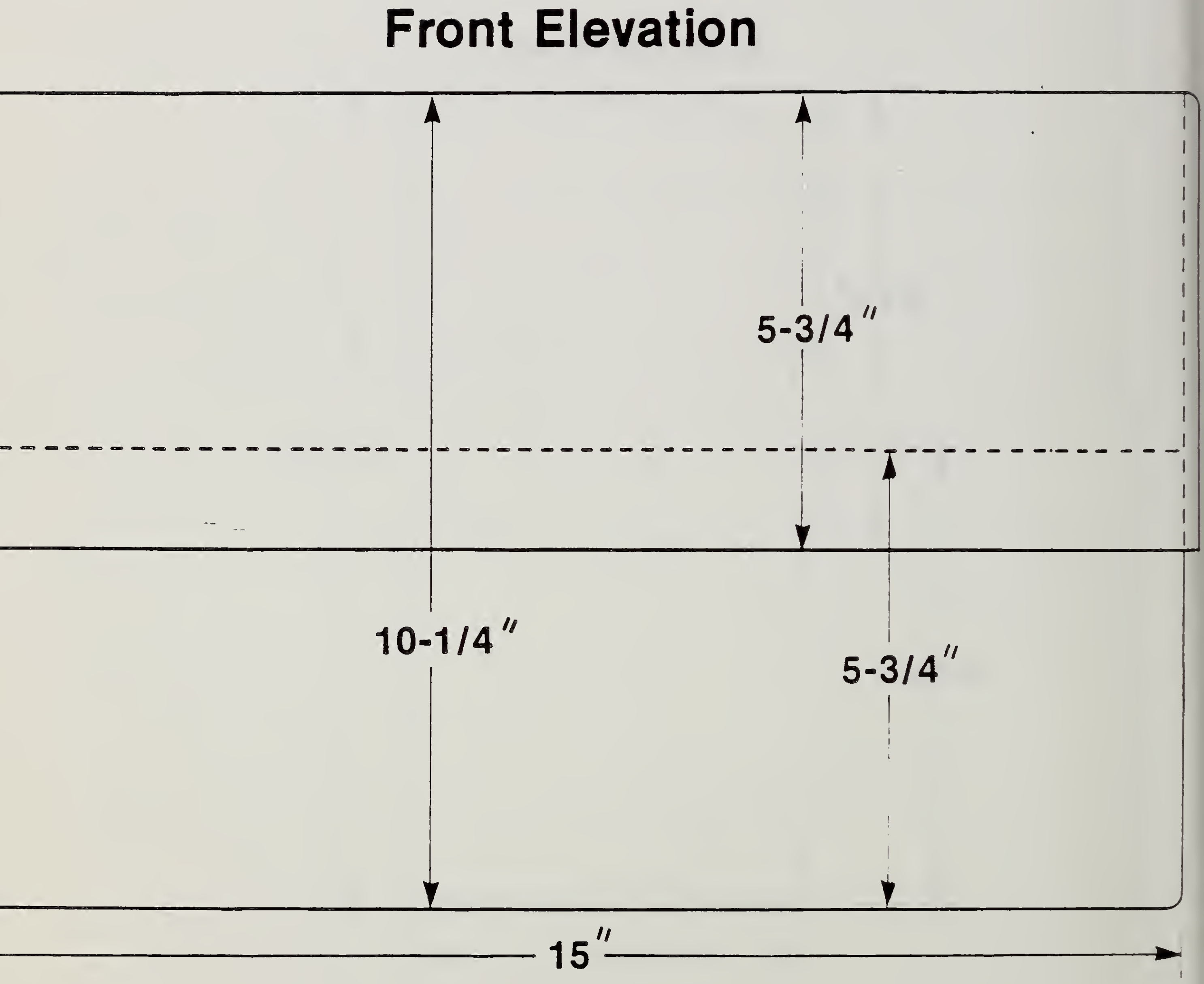
10. Same as Fig.9, but diffusion is through gaps.

Fig. 1a



(a)

Fig. 1b



(b)

Fig. 2

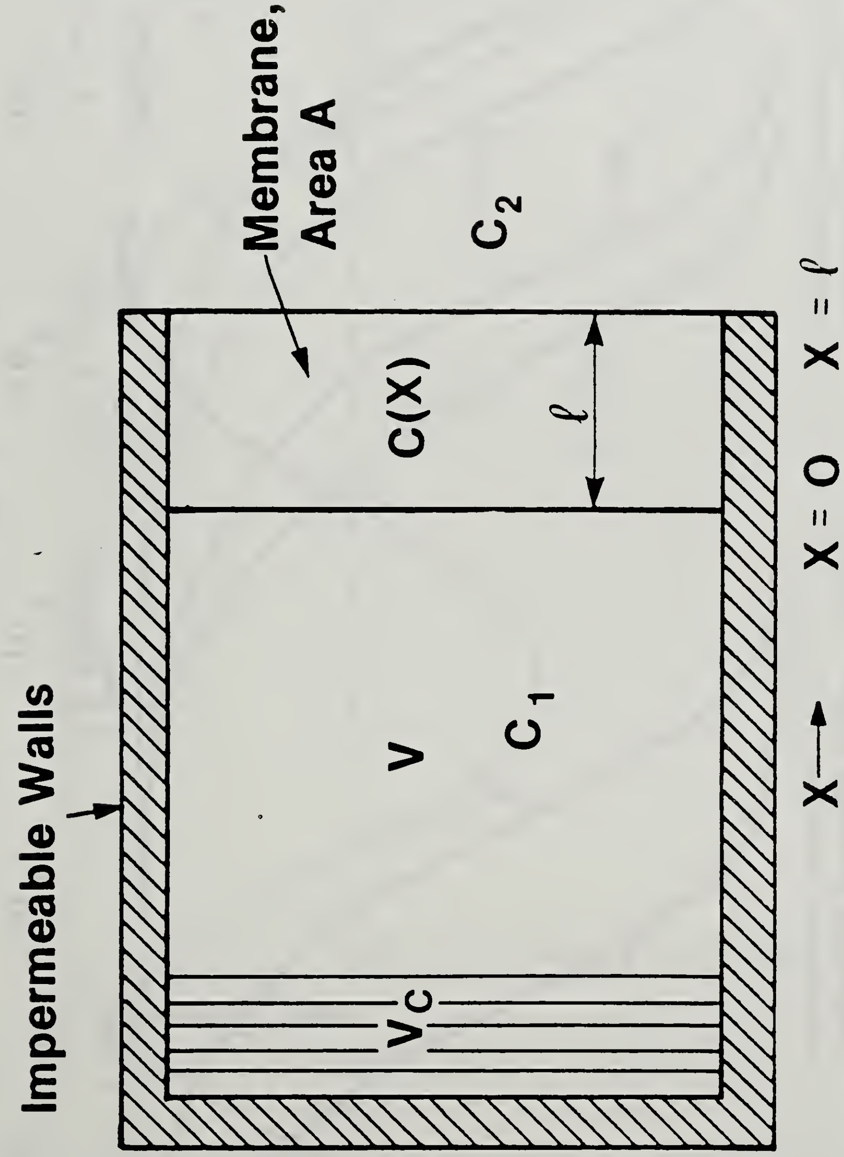

Impermeable Walls
Membrane, Area A
C_2
$C(X)$
ℓ
V
C_1
V_C
$X \rightarrow$
$X = O$
$X = \ell$

Fig. 3

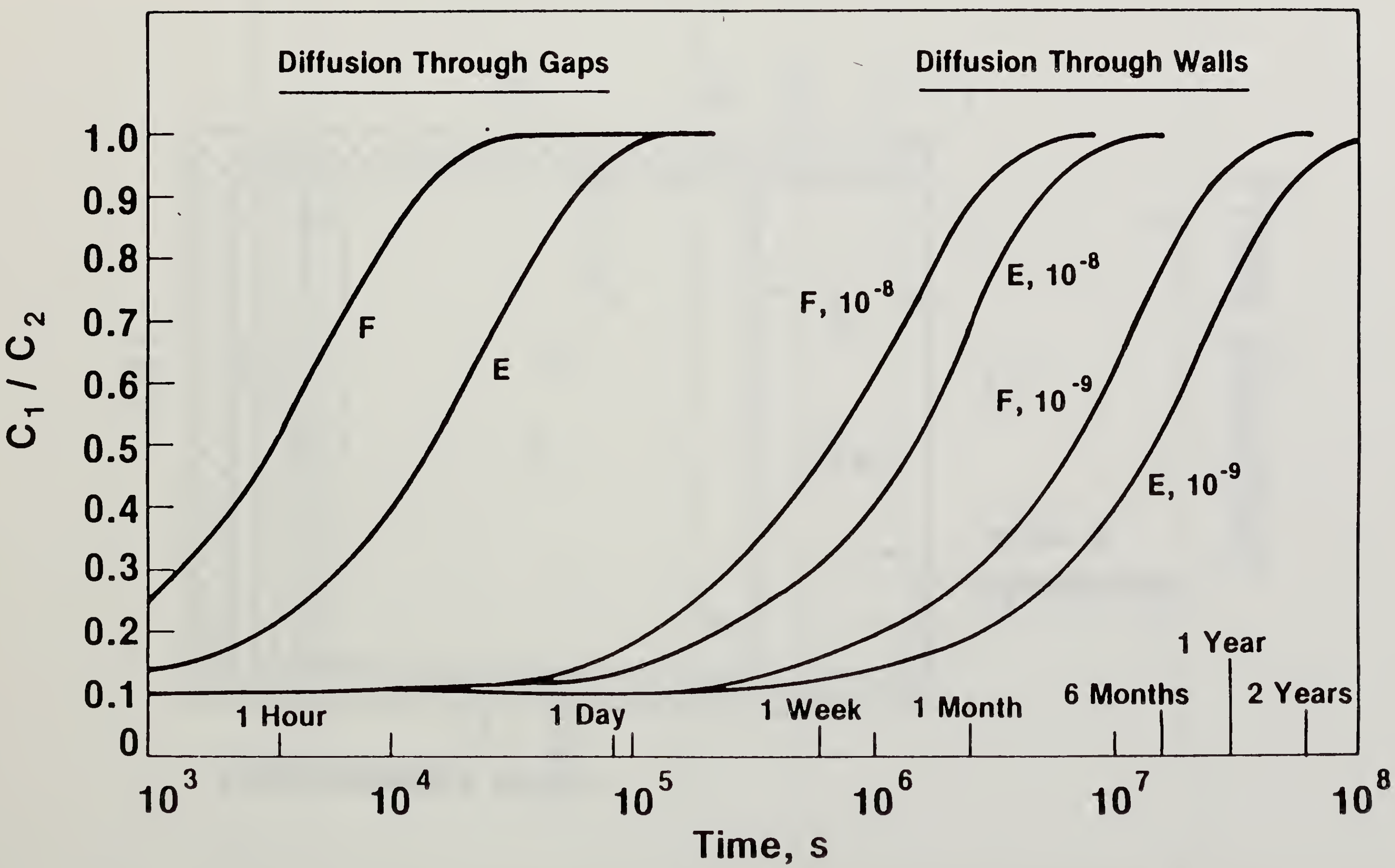

Diffusion Through Gaps
Diffusion Through Walls
C_1 / C_2
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
F
E
F, 10^{-8}
E, 10^{-8}
F, 10^{-9}
E, 10^{-9}
1 Hour
1 Day
1 Week
1 Month
6 Months
1 Year
2 Years
10^3
10^4
10^5
10^6
10^7
10^8
Time, s

Fig.4

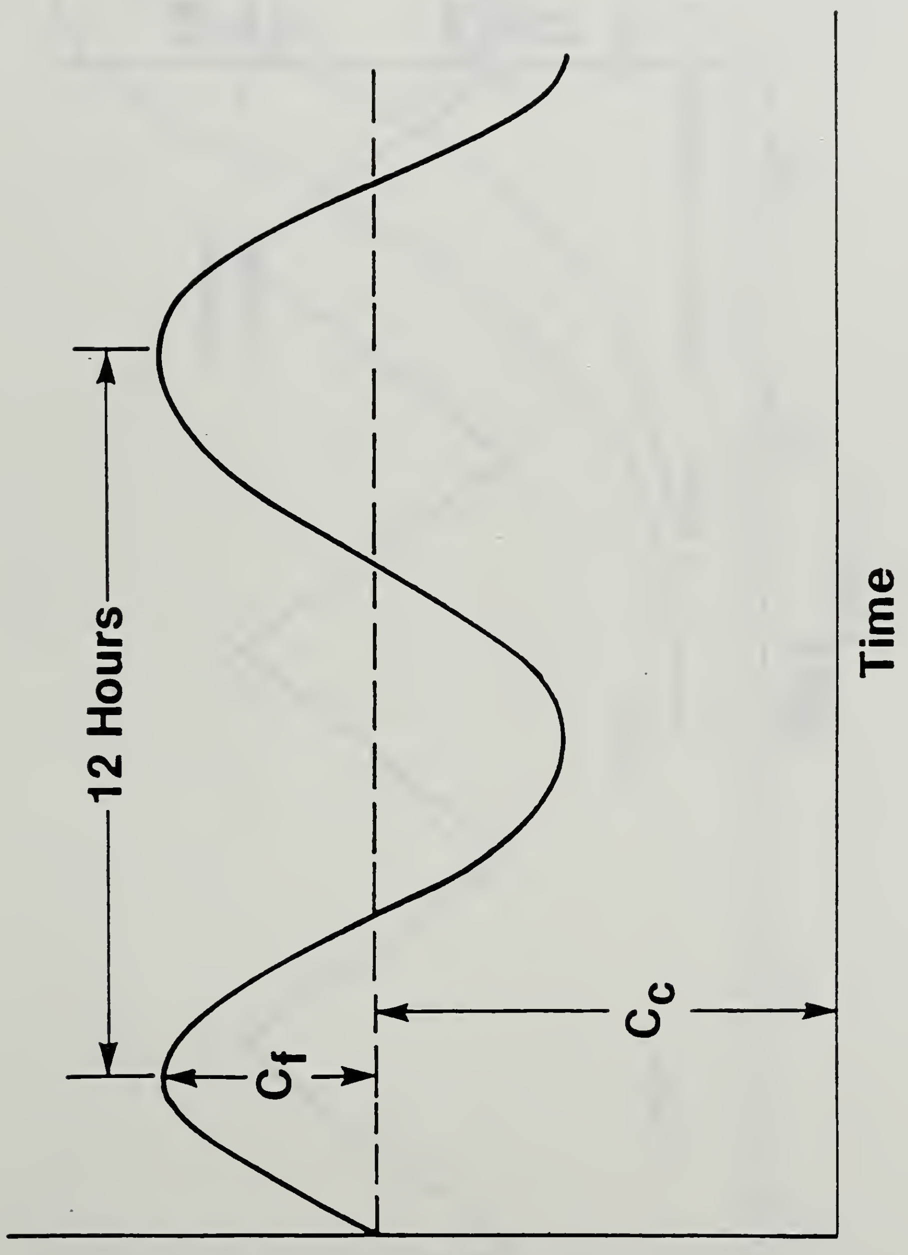


Fig. 5

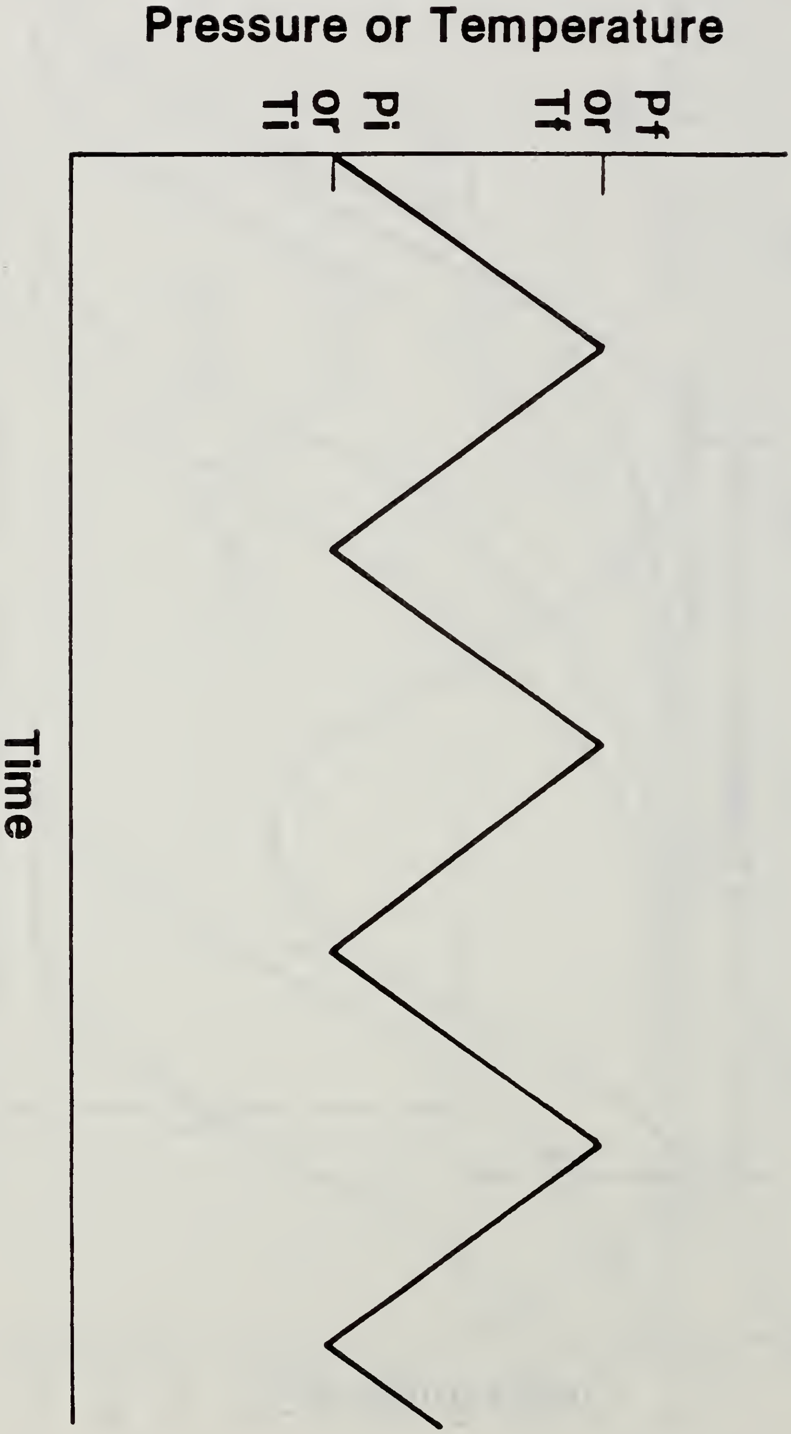
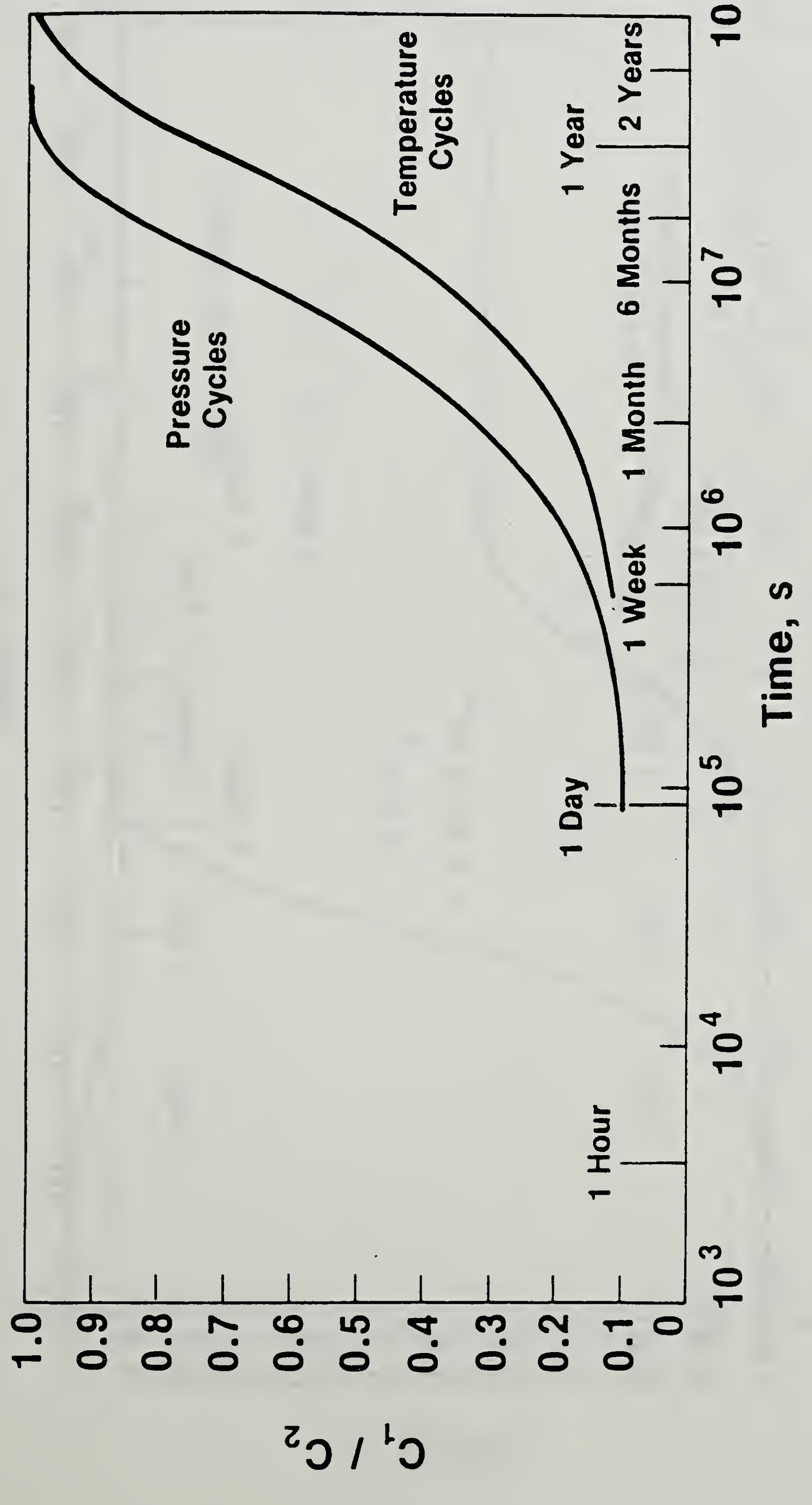


Fig. 6



C₁ / C₂
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Time, s
10³
10⁴
10⁵
10⁶
10⁷
10⁸
1 Hour
1 Day
1 Week
1 Month
6 Months
1 Year
2 Years
Pressure Cycles
Temperature Cycles

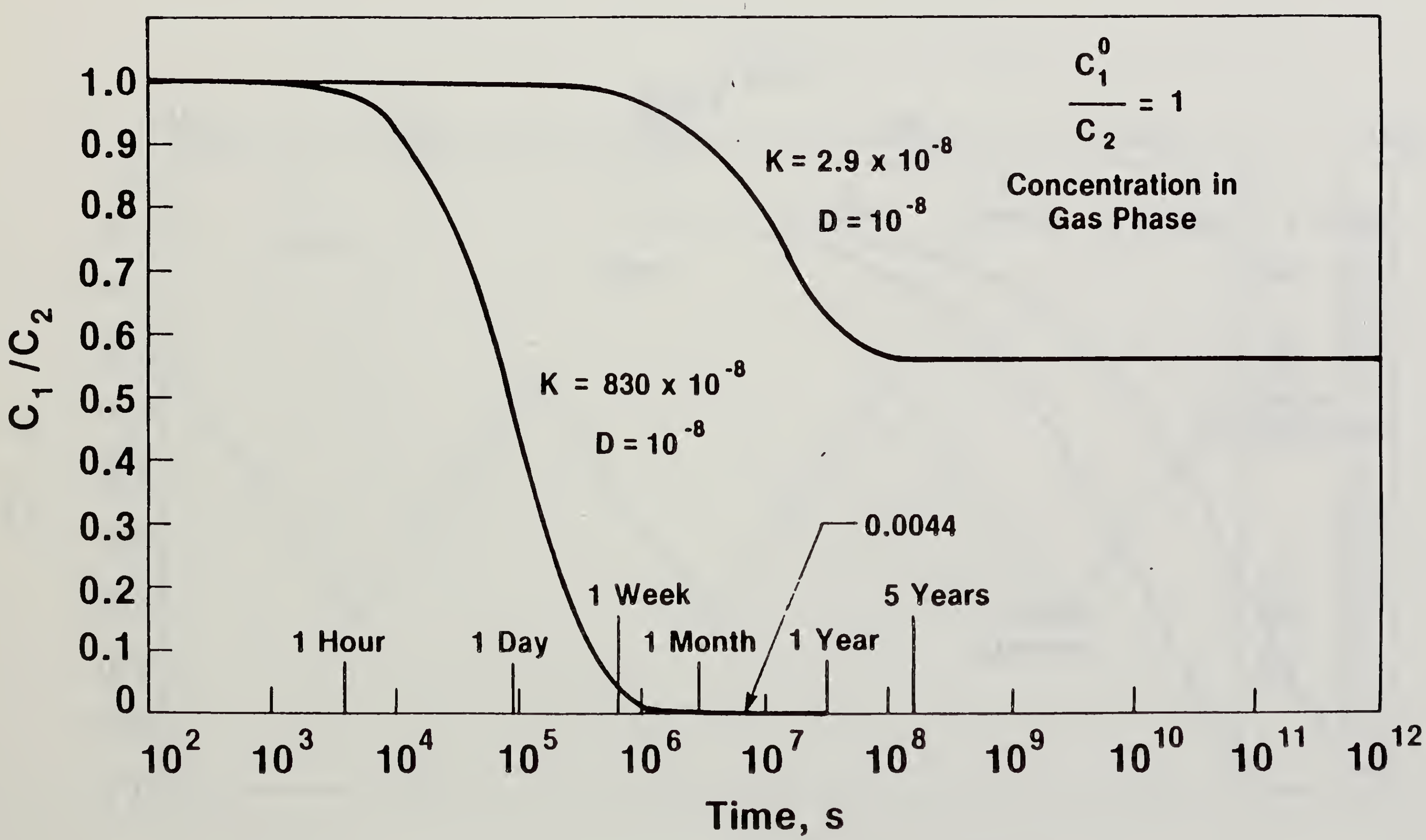

$\frac{C_1^0}{C_2} = 1$
Concentration in Gas Phase
K = 2.9 x 10^{-8}
D = 10^{-8}
K = 830 x 10^{-8}
D = 10^{-8}
0.0044
1 Hour
1 Day
1 Week
1 Month
1 Year
5 Years
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
C_1 / C_2
10^2
10^3
10^4
10^5
10^6
10^7
10^8
10^9
10^{10}
10^{11}
10^{12}
Time, s

Fig. 7

Fig. 8

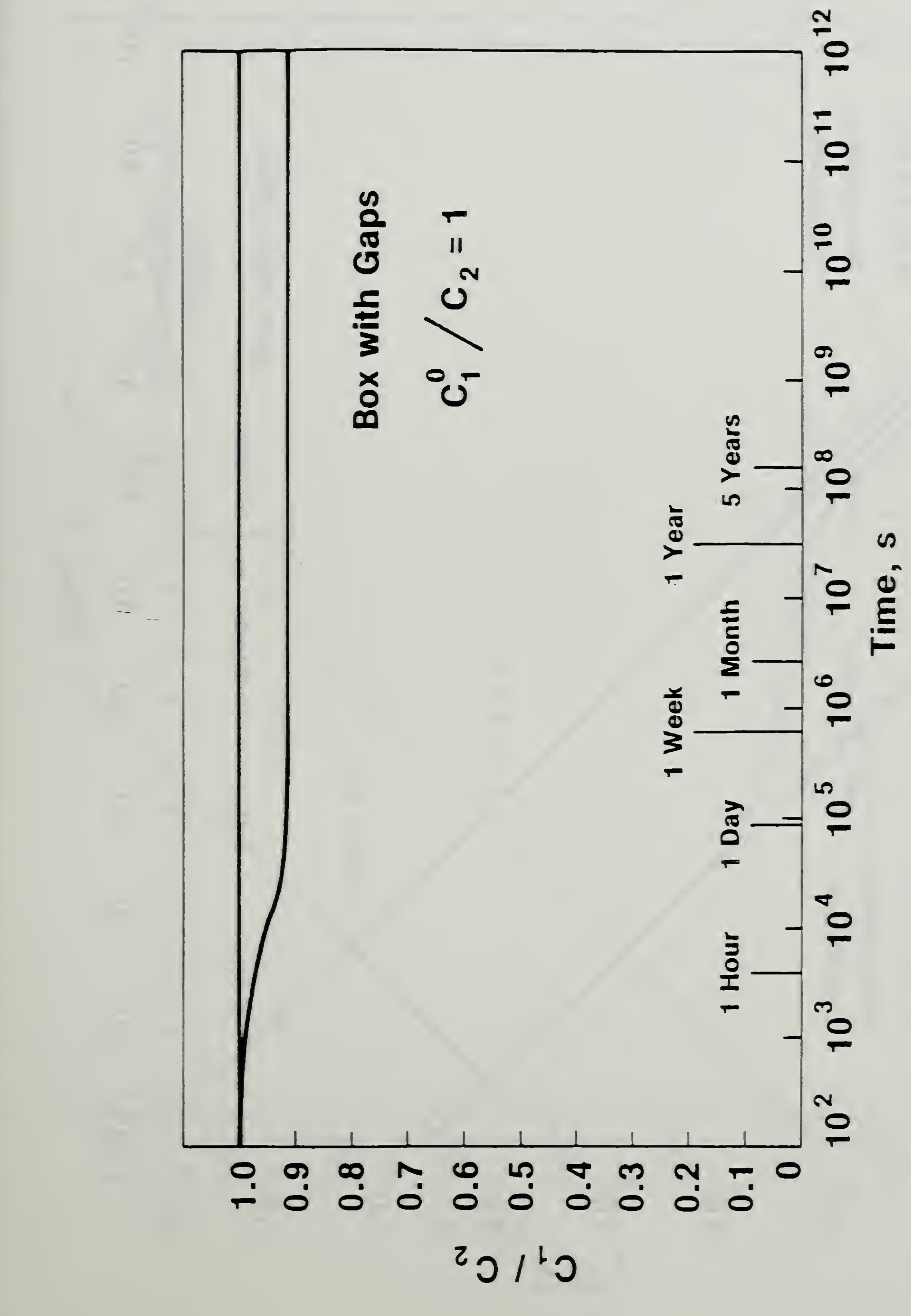
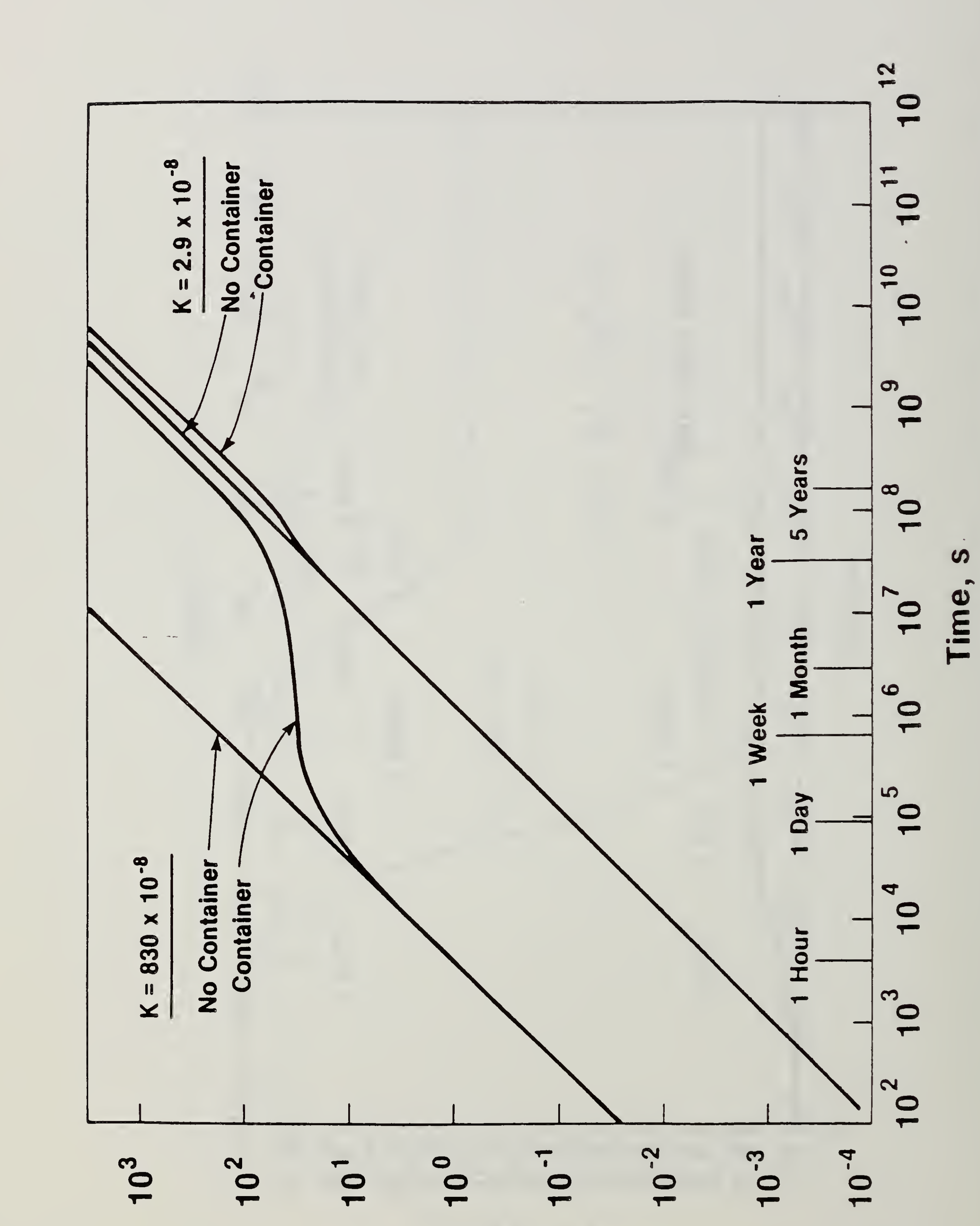
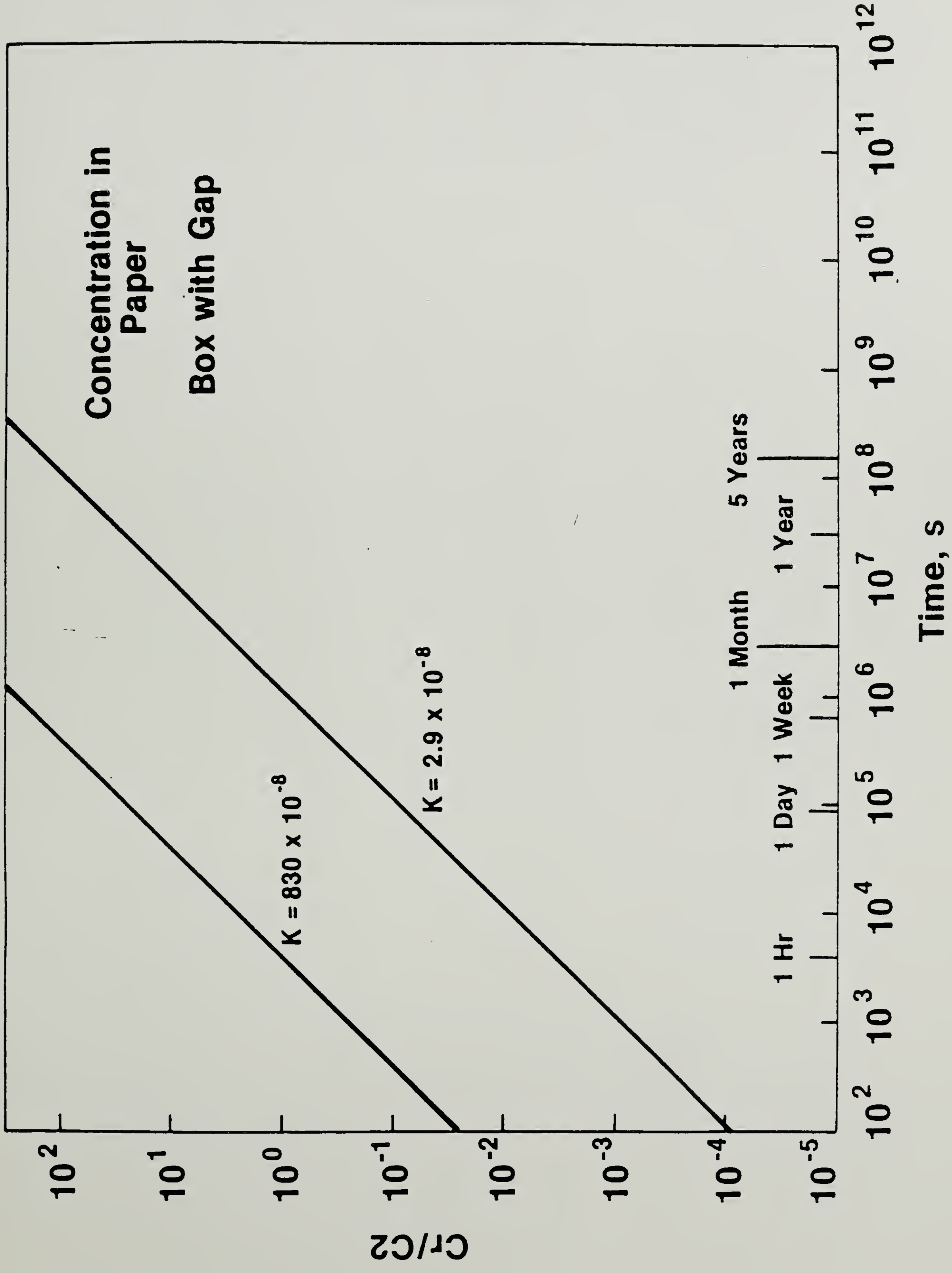

Box with Gaps
$C_1^0 / C_2 = 1$
C_1 / C_2
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Time, s
10^2
10^3
10^4
10^5
10^6
10^7
10^8
10^9
10^{10}
10^{11}
10^{12}
1 Hour
1 Day
1 Week
1 Month
1 Year
5 Years

Fig. 9



C_r/C_2
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
10^{7}
10^{8}
10^{9}
10^{10}
10^{11}
10^{12}
Time, s
1 Hour
1 Day
1 Week
1 Month
1 Year
5 Years
K = 830 x 10^{-8}
No Container
Container
K = 2.9 x 10^{-8}
No Container
Container

Fig. 10


Concentration in Paper
Box with Gap
K = 830 x 10^{-8}
K= 2.9 x 10^{-8}
Cr/C2
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
Time, s
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
10^{7}
10^{8}
10^{9}
10^{10}
10^{11}
10^{12}
1 Hr
1 Day
1 Week
1 Month
1 Year
5 Years

APPENDICES

Appendix A-1

In problems involving diffusion, and particularly when reactions are involved, the questions of units and dimensions arise, and can often cause confusion. In this Appendix, the conventions adopted in this report are given. In addition, a material balance problem that arises when diffusion accompanied by reaction occurs will be stated and solved. It is hoped that this will alleviate, if not completely remove, questions that may arise in the treatments of models to follow.

A. Definitions and Conventions

1. D is the diffusion constant. It has units cm^2/sec.
2. C is concentration. It has dimensions amount/volume. Because we will need to be concerned with concentration of gases or vapors, we will always express "amount" as cm^3 (STP). Thus, for the gas phase the concentration units will be cm^3/cm^3, which is the same as mole fraction in the ideal gas approximation, which is always used. Note that this is not a useful definition for gases unless the total pressure is specified. In all the cases of concern in this report the total pressure is always one atmosphere so that the definition is useful. Considering the data availability and quality, small differences from standard conditions are ignorable. For concentration in the solid phase we will use cm^3 STP/cm^3, i.e., the amount of material expressed as cm^3 at Standard Temperature and Pressure per cm^3.

   We shall often be concerned with concentration inside and outside a container, and concentration in the solid phase (usually the walls or contents of a container). We shall always denote the interior concentration by C_1 and the exterior by C_2, except in special circumstances.

The concentration in the solid phase will always be denoted by C, using subscripts to denote more specific details about the phase.

3. S denotes the solubility coefficient. It is defined as

$$S = \frac{C_s}{C_g} \qquad 1\text{-}1$$

where C_s and C_g are concentrations in the solid and gas phase, respectively. Hence, with our definition for concentration, S is dimensionless. Again, this is only useful at a specified total pressure, which is always one atmosphere in the report. The small difference between STP and the actual conditions is ignored since we know the values of these quantities so poorly.

4. k is a first order reaction rate constant. It has units sec^{-1}.

5. V is the volume of a container <u>accessible to a pollutant</u>. Thus it consists of the unoccupied volume plus the "solution volume" of the contents. Thus, if V_u is the unoccupied volume and V_c is the physical volume of the contents, then

$$V = V_u + SV_c \qquad 1\text{-}2$$

Its units are cm^3.

6. A is the area of a container by which pollutant has access to V. Its units are cm^2.

7. ℓ is the thickness of the walls of a container. Its units are cm.

With these conventions and definitions, the flux of pollutant into a box (see subsequent appendices) is in cm^3/cm^2 sec.

B. A Mass Balance Problem

We shall have occasion to be concerned with a container containing reactive contents and into which there is a flux of pollutant. The pollutant is soluble in the contents, but the rate of solution is rapid, so the reaction is not diffusion limited. The contents react with the pollutant by a first order reaction. We do a mass balance.

First, consider the contents. There will be some pollutant in solutions, and some reacted pollutant. Let the total amount in the contents be A_c. Then

$$A_c = A_S + A_r \tag{1-3}$$

where A_S is the amount of pollutant in solution and A_r the amount reacted (i.e. "fixed" or converted.) Then

$$\frac{dA_c}{dt} = \frac{dA_S}{dt} + \frac{dA_r}{dt} \tag{1-4}$$

Now, if V_C is the volume of contents and C_S and C_r the respective concentrations in amount/volume, this becomes

$$\frac{dA_c}{dt} = V_c \frac{dC_S}{dt} + V_c \frac{dC_r}{dt} \tag{1-5}$$

Now consider the fluid phase in the container. By similar reasoning we have

$$\frac{dA_f}{dt} = V_f \frac{dC_f}{dt} \tag{1-6}$$

If there is a total flux F of pollutant into the container, then clearly

$$\begin{aligned} F &= \frac{dA_f}{dt} + \frac{dA_c}{dt} \\ &= V_f \frac{dC_f}{dt} + V_c \frac{dC_S}{dt} + V_c \frac{dC_h}{dt} \end{aligned} \tag{1-7}$$

By definition, and the assumption that solution is rapid, $C_S = SC_f$, hence

$$F = V_f \frac{dC_f}{dt} + V_c S \frac{dC_f}{dt} + V_c \frac{dC_r}{dt} \tag{1-8}$$

or since $V = V_f + V_c S$,

$$F = V \frac{dC_f}{dt} + V_c \frac{dC_r}{dt} \qquad (1\text{-}9)$$

This an equation we shall have occasion to use.

We can, however, go further. For a first order reaction, we have

$$\frac{dC_r}{dt} = k\ C_S \qquad (1\text{-}10)$$

or

$$V_c \frac{dC_r}{dt} = V_c kSC_f \qquad (1\text{-}11)$$

which we shall also have occasion to use in calculating the extent of reaction in the contents. Note that with our previous definitions, $C_f = C_1$.

Appendix A-2

Diffusion Into an Empty Container or a Container Holding Inert Documents-Exact Solution.

Referring to Fig. 2 of the text, we have this boundary value problem:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2} \qquad (2\text{-}1)$$

$$C(X,0) = C_o(X\ ) \qquad (2\text{-}2)$$

$$C(0,t) = SC_1(t);\ C_1(0) = C_1{}^{\circ} \qquad (2\text{-}3)$$

$$C(\ell,t) = SC_2 \qquad (2\text{-}4)$$

$$\frac{dC_1}{\partial t} = \frac{AD}{V}\ \frac{\partial C}{\partial X}\bigg|_{X=0} \qquad (2\text{-}5)$$

where S is the solubility coefficient. It is assumed that the interior concentration, C_1, is not dependent on position (i.e., it is "stirred"). The solution is based upon those given by Barnes (23) and March and Weaver (24).

Let $C = C' + C''$ (2-6)

Where C' satisfies (2-2) and is zero at $X=0$ and $X=\ell$.

Then

$$C' = \sum_{1} C_n \exp(-\alpha_n t)\ \text{Sin}\ \frac{n\pi x}{\ell} \qquad (2\text{-}7)$$

$$\alpha_n = \frac{Dn^2\pi^2}{\ell^2} \qquad (2\text{-}8)$$

$$C_n = \frac{2}{\ell} \int_0^{\ell} C_o(x)\ \text{Sin}\ \frac{n\pi x}{\ell} \qquad (2\text{-}9)$$

Following Carslaw and Jaeger, ((1) p. 102) C" is obtained from

$$\frac{C''}{S} = \int_0^t \left[\ C_1(t)\frac{\partial}{\partial t}F_1(t-\tau)+C_2\frac{\partial}{\partial t}F_3(t-\tau)\ \right]d\tau \qquad (2\text{-}10)$$

where

$$F_1 = 1 - \frac{x}{\ell} - \frac{2}{\pi} \sum \frac{1}{n}\text{Sin}\ \frac{n\pi x}{\ell}\ \exp\ [-\alpha_n t] \qquad (2\text{-}11)$$

$$F_2 = \frac{x}{\ell} + \frac{2}{\pi} \sum(-)^n \frac{1}{n} \mathrm{Sin} \frac{n\pi x}{\ell} \exp\ [-\alpha_n t] \tag{2-12}$$

Eq. 10 can be transformed to

$$\frac{C''}{S} = C_1{}^{\circ} F_1(x,t) + C_2 F_2(x,t)$$

$$+ \int_0^t \left[C_1{}'(\tau) F_1(X,t-\tau) + C_2{}'(\tau) F_2(x,t-\tau) \right] d\tau \tag{2-13}$$

where the prime on C_1 and C_2 denote differentiation. Now sum Eq. 7 and Eq. 13, differentiate with respect to x, and take the limit as $x \to 0$. Then use Eq. 2-5 to obtain

$$\frac{\ell V}{ADS} \frac{\partial C_1}{\partial t} = C_2 - C_1 - 2\sum D_n \exp.[-\alpha_n t]$$

$$- 2 \sum \int C_1{}^1\ (t) \exp.\ [-\alpha_n(t-\tau)\ |dt \tag{2-14}$$

with

$$D_n = C_1{}^{\circ} - (-)^n C_2 - \frac{n\pi}{2} C_n \tag{2-15}$$

Eq. 2-14 is an integro-differential equation for C_1. It may be solved as follows. Assume $C_1{}'$ may be written as a series of exponentials:

$$C_1{}' = A_i \sum_i \exp.\ (-\xi_i t) \tag{2-16}$$

We know that as $t \to \infty$, $C \to C_2$, and hence

$$C_1(t) = C_2 - \sum \frac{A_i}{\xi_i} \exp\ (-\xi_i t) \tag{2-17}$$

Substituting Eq. 2-16 into Eq. 2-14 leads to the following:

$$\frac{\ell V}{ADS} - \frac{1}{\xi_i} + 2 \sum_n \frac{1}{\alpha_n - \xi_i} = 0 \tag{2-18}$$

and

$$D_n = C_1(o) - (-)^n C_2 - \frac{n\pi}{2} C_n = \sum \frac{A_i}{\alpha_n - \xi_i} \tag{2-19}$$

Eqs. 2-18 and 2-19 form an infinite set of non linear equations for the ξ_i and A_i. Eq. 2-18, however may be transformed as follows. Define

$$Z_i{}^2 = \xi_i \ell^2 / D \tag{2-20}$$

then it may be shown that Eq. (2-18) for the ξ_i results in the following

$$\frac{V}{A\ell S} - \frac{\text{Cot } Z_i}{Z_i} = 0 \qquad (2\text{-}21)$$

The scheme for the solution is now clear. It goes as follows.

1) A, D, V, ℓ and S are assumed known, as are the exterior concentration C_2 the interior concentration $C_1°$, and the concentration profile C(x) in the container walls when the container is closed.

2) From C(x) calculate C_n by Eq. 2-9.

3) From these and C_2 and $C_1°$, calculate D_n by Eq. 2-19.

4) With the values of D, V, ℓ, A and S calculate the roots of Eq. 2-19, and hence the ξ_i.

5) With these, calculate the A_i from Eqs. 2-19. One trial has shown that three of these are sufficient to get a good approximate solution.

6) Having the A_i and ξ_i, Eq. 2-17 gives the time dependence of C_1.

This is clearly a rather tedious procedure, but it is amenable to programming on a computer.

Appendix A-3

Diffusion Into an Empty container or a Container Holding Inert Documents - Approximate Solution, Constant Exterior Concentration

The situation is the same as in A-1, but we make the approximation that the concentration in the membrane varies linearly with position. The flux of pollutant into the container is then

$$F = D \frac{C(\ell) - C(o)}{\ell} \qquad (3\text{-}1)$$

where $C(\ell)$ and $C(o)$ are the concentrations in the membrane at $x = \ell$ and $x = o$ respectively. These are related to the concentration in the gas phase by

$$C(\ell) = SC_2 \qquad (3\text{-}2)$$

$$C(o) = SC_1 \qquad (3\text{-}3)$$

where S is the solubility coefficient, and is assumed to be independent of concentration. For diffusion through gaps, clearly S=1. Then, the rate of change of concentration in the interior of the container is

$$\frac{\partial C_1}{\partial t} = \frac{ADS}{V\ell} (C_2 - C_1) \qquad (3\text{-}4)$$

Since for this case C_2 is a constant, this equation has the solution

$$C_1 = C_2 - (C_2 - C_1°) \exp(-t/\tau) \qquad (3\text{-}5)$$

or

$$C_1/C_2 = 1 - (1 - C_1°/C_2) \exp(-t/\tau) \qquad (3\text{-}6)$$

where $C_1°$ is the initial concentration inside the container (i.e., when it is closed or placed into an atmosphere of concentration C_2) and τ is given by

$$\tau = \frac{V\ell}{ADS} \qquad (3\text{-}7)$$

Hence τ serves the function of a relaxation time. It depends upon the design of the container via V, A and ℓ, and upon the material of construction via D and S.

Appendix A-4

Diffusion Into an Empty Container or a Container Holding Inert Documents - Approximate Solution, Varying Exterior Concentration.

This model is the same as that in A-2 except that the exterior concentration varies with time. Referring to Fig. 4, we take it to be

$$C_2 = C_c + C_f \sin \omega t \tag{4-1}$$

where ω is the angular frequency of the variation, i.e., 2π/period. The differential equation for the rate of change of interior concentration then becomes

$$\frac{\partial C_1}{\partial t} = \frac{ADS}{V\ell} (C_c + C_f \sin \omega t - C_1) \tag{4-2}$$

where the terms have the same meaning as before (See A-1, A-2, Fig. 2). This equation is solved by standard methods to give

$$C_1 = \alpha \exp(-t/\tau) + C_c + \frac{C_f \mathrm{Sin}(\omega t+\delta)}{1+\omega^2\tau^2} \tag{4-3}$$

where again $\tau = V\ell/ADS$, $\tan\delta = -w\tau$, and α is a constant to be determined by the initial condition. Thus, at t = o we obtain

$$C_1{}^{\circ} = \alpha + C_c + \frac{C_f \mathrm{Sin}\delta}{1+\omega^2\tau^2} \tag{4-4}$$

The last term will be small if $\omega\tau >> 1$ or $\omega\tau << 1$. This is the situation for the cases investigated. Moreover, even if this were not the case, it would only be necessary to take the zero of time a little differently in order to ignore the last term. Hence it is dropped, and with this approximation the final result is

$$\frac{C_1}{C_c} = 1 - \left(1 - \frac{C_1{}^{\circ}}{C_c}\right) \exp(-t/\tau) + \frac{C_f}{C} \frac{\mathrm{Sin}(\omega t+\delta)}{1+\omega^2\tau^2} \tag{4-5}$$

Appendix A-5

Flows Through Gaps by Pressure and Temperature Changes - The "Breathing" Modes.

Consider a container of volume V containing gas, which is assumed to be ideal. The moles of gas in the container is given by

$$n = PV/RT \tag{5-1}$$

where P is the pressure, T the temperature and R the gas constant. Since V is a constant, n will change as P and T change.

$$\frac{dn}{n} = \frac{dP}{P} - \frac{dT}{T} \tag{5-2}$$

This equation shows that an increase in pressure and a decrease in temperature both increase the amount of gas in the box. This can only come about by drawing in gas from the exterior. This gas will carry pollutant with it, and if the concentration of the exterior gas is different from the interior, the interior concentration will be changed. Conversely, as the pressure decreases or this temperature increases, gas will be exhausted, but this will not change this concentration.

We now solve for the concentration changes. In what follows, concentration will be expressed as mole fraction, X, which is the same as volume fraction, C. Inside the container, let the number of moles of pollutant be n_{1a} and the sum of all other species be n_{1b}. Then the mole fraction of pollutant is

$$X_{1a} = \frac{n_{1a}}{n_{1a}+n_{1b}} \tag{5-3}$$

and

$$n = n_{1a} + n_{1b} \tag{5-4}$$

From Eq. 5-3 we obtain

$$dX_{1a} = \frac{dn_{1a}}{n} - X_{1a}\frac{dn}{n} \tag{5-5}$$

But dn_{1a} is just the number of moles of pollutant carried in by exterior gas. Hence we have

$$dn_{1a} = X_{2a}dn \tag{5-6}$$

where X_{2a} is the concentration of pollutant in the exterior. Hence we obtain

$$dX_{1a} = (X_{2a} - X_{1a})\frac{dn}{n} \tag{5-7}$$

Now assume that only the pressure has changed. Then, using Eq. 5-2 we obtain

$$\frac{dX_{1a}}{X_{2a} - X_{1a}} = \frac{dP}{P} \tag{5-8}$$

Consider now that we are undergoing pressure cycles as shown in Fig. 5. We integrate Eq. 5-8 from the start of the i'th increase to its end, which we call i+1. Then we obtain

$$-\ell n\,\frac{X_{2a}-X_{1a,i+1}}{X_{2a}-X_{1a,i}} = \ell n\,\frac{P_{i+1}}{P_i} \tag{5-9}$$

For the next cycle we obtain

$$-\ell n\,\frac{X_{2a}-X_{1a,i+2}}{X_{2a}-X_{1a,i+1}} = \ell n\,\frac{P_{i+2}}{P_i} \tag{5-10}$$

But the pressure change is the same for all cycles. Hence by summing Eqs. 5-9 and 5-10 we obtain

$$-\ell n\,\frac{X_{2a}-X_{1a,i+2}}{X_{2a}-X_{1a},i} = 2\ell n\,\frac{P_f}{P_i} \tag{5-11}$$

where P_f and P_i are the pressures at the end and beginning of the pressure rise. Clearly, if we start with the first and carried out N pressure cycles we obtain

$$-\ell n \frac{X_{2a} - X_{1a,N}}{X_{2a} - X_{1a,1}} = N \ell n \frac{P_f}{P_i} \tag{5-12}$$

This can be solved for X_{1a},N to give

$$X_{1a,N} = X_{2a} - (X_{2a} - X_{1a,1}) \left(\frac{P_i}{P_f}\right)^N \tag{5-13}$$

Recalling that volume fraction is the same as mole fraction, we obtain

$$\frac{C_1}{C_2} = 1 - (1 - \frac{C_1°}{C_2}) \left(\frac{P_i}{P_f}\right)^N \tag{5-14}$$

For temperature cycles, the analysis proceeds in exactly the same manner, but because of the minus sign in Eq. 5-2, the result is

$$\frac{C_1}{C_2} = 1 - (1 - \frac{C_1°}{C_2}) \left(\frac{T_f}{T_i}\right)^N \tag{5-15}$$

Eqs. 5-14 and 5-15 are those discussed in the text.

Appendix A-6

The Container with Reactive Contents - Exact Solution

This solution follows in exact parallel the solution in Appendix A-2. The only difference is in Eq. 2-5 of that Appendix. Hence we have the following boundary value problems

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{6-1}$$

$$C(x,o) = C_o(x) \tag{6-2}$$

$$C(o,t) = SC_1(t); \; C_1(o) = C_1{}^{\circ} \tag{6-3}$$

$$C(\ell,t) = SC_2 \tag{6-4}$$

$$\frac{\partial C_1}{\partial t} = \frac{AD}{V} \frac{\partial C}{\partial x}\bigg|_{x=0} - \frac{V_c k S C_1}{V} \tag{6-5}$$

The final equation follows the material balance considerations given in A-1. It simply states that the rate of change of concentration is the difference between the flux of pollutant into the container and the rate at which it reacts with the contents.

Proceeding as in A-1, we obtain

$$\frac{V\ell}{ADS} \frac{\partial C_1}{\partial t} + \frac{V_c k \ell C_1}{AD} = C_2 - C_1 - 2\sum D_n \exp(-\alpha_n t)$$
$$-2\sum \int C' \exp[-\alpha_n (t-\tau)] \, d\tau \tag{6-6}$$

This is an integro-differential equation for C_1. Again we let

$$\frac{dC_1}{dt} = \sum A_i e^{-t\xi i} \tag{6-7}$$

giving

$$C_1 = C_1^{\infty} - \sum \frac{A_i}{\xi_i} e^{-t\xi_i} \qquad (6\text{-}8)$$

where C_1^{∞} now is not C_2, but the steady state value of C_1. Substituting Eqs. 6-7 and 6-8 into Eq. 6-6 we obtain

$$D_n = \sum_i \frac{A_i}{\alpha_n - \xi_i} \qquad (6\text{-}9)$$

and

$$\frac{V\ell}{DAS} - \frac{1}{\xi_i}\left[\frac{V_c k\ell}{DA} + 1\right] + 2\sum_n \frac{1}{\alpha_n - \xi_i} = 0 \qquad (6\text{-}10)$$

where D_n, as in A-2 is

$$D_n = C_1^{\circ} - (-)^n C_2 - \frac{n\pi}{2} C_n \qquad (6\text{-}11)$$

Equations (6-9) and 6-10 are again infinite sets of non-linear equations for the A_i and ξ_i. Proceeding as before, Eq. 6-10 maybe simplified. Again define

$$Z_i^2 = \xi_i \ell^2/D \qquad (6\text{-}12)$$

A certain amount of manipulation now yields an equation for the Z_i and hence the ξ_i:

$$\frac{V}{\ell AS} - \frac{V_c \ell k}{DA}\,\frac{1}{Z_i^2} = \frac{\text{Cot } Z_i}{Z_i} \qquad (6\text{-}13)$$

This equation can very likely be solved for the Z_i by numerical methods, but this was not attempted. The scheme for the solution would proceed as in A-2.

Appendix A-7

The Container With Reactive Contents- Approximate Solution

As in A-2, we assume that the concentration in the walls of the container varies linearly with position. It is assumed that diffusion into the contents is rapid so that their reaction with the pollutant is not controlled by the rate of diffusion into them. This will be approximated more closely if the contents are not tightly packed. Then, equating the rate of change of concentration inside the container to the flux into it minus the rate of reaction with the contents, as described in A-1, we obtain

$$\frac{dC_1}{dt} = \frac{ADS}{V\ell} (C(\ell) - C(o)) - \frac{V_c k C_h}{V} \tag{7-1}$$

and from the definition of S in A-1,

$$\frac{\partial C_1}{\partial t} = \frac{ADS}{V\ell} (C_2 - C_1) - \frac{V_c kSC_1}{V} , \tag{7-2}$$

where it has been assumed that the solubility coefficient for the contents is the same as for the walls. This is obviously easily rectified.

Eq. 7-2 is a differential equation for C_1. It is solved by standard means to yield, for C_2 a constant,

$$\frac{C_1}{C_2} = \frac{1}{1+\tau_1/\tau_2} + \left[\frac{C_1{}^{\circ}}{C_2} - \frac{1}{1+\tau_1/\tau_2}\right] \text{exp.} \left[-(\frac{1}{\tau_1} + \frac{1}{\tau_2})t\right] \tag{7-3}$$

where $\tau_1 = V\ell/ADS$ and $\tau_2 = V/V_c kS$.

This equation is very similar to Eq. 3-6 of A-3. Only the factor τ_1/τ_2 and the factor in the argument of the exponential term make it different. An important point is to notice that the relaxation time for this process is <u>smaller</u> than either τ_1 or τ_2. If we denote the relaxation time by τ_S, then it follows directly that

$$\tau_S = \frac{\tau_1 \tau_2}{\tau_1 + \tau_2} \tag{7-4}$$

which is smaller than either τ_1 or τ_2. Further details of the behavior are given in the text.

The increase of concentration of reacted pollutant in the contents is easily calculated from these results. From the first order reaction we have, following Appendix 1,

$$\frac{dC_r}{dt} = k\ C_c \tag{7-5}$$

where C_r is the concentration of reacted pollutant in the contents and Cc is the concentration of <u>unreacted</u> pollutant.

But since $Cc = SC_1$, we obtain

$$C_r - C_r^\circ = \frac{kSC_2 t}{1+\tau_1/\tau_2} - \frac{kS}{(1/\tau_1+1/\tau_2)} \left[C_1^\circ - \frac{C_2}{1+\tau_1/\tau_2} \right] \left\{ \exp\left[- \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} \right) t \right] - 1 \right\} \tag{7-6}$$

where C_r° is the concentration of reacted pollutant at the initial time. An important point is that after a very long time and the exponential term has become negligible, reaction continues. This is discussed more fully in the main text.

Appendix A-8

Container with Reactive Contents - Approximate Solution, Time Varying Exterior Concentration

This model is treated in exact parallel with A-7, except that the exterior concentration now varies with time. Assuming the time variation to be as in A-4, we obtain for the basic differential equation for the concentration inside the container.

$$\frac{\partial C_1}{\partial t} = \frac{ADS}{V\ell}\left(C_c + C_f \mathrm{Sin}\omega t - C_1\right) - \frac{V_c kS}{V} C_1 \qquad (8\text{-}1)$$

where all the symbols have been previously defined. This differential equation is easily solved by standard methods to yield

$$C_1 = \alpha e^{-t/\tau_s} + \frac{C_c}{1+\tau_1/\tau_2} + \frac{C_f}{1+\tau_1/\tau_2}\,\frac{\mathrm{Sin}(\omega t+\delta)}{1+\omega^2\tau^2} \qquad (8\text{-}2)$$

where α is a constant to be determined by the initial conditions, and $\tau_s = \tau_1\tau_2/\tau_1+\tau_2$. Using the same approximations as in A-4, we obtain

$$\frac{C_1^{\circ}}{C_c} = 1 - \left(1 - \frac{C_1^{\circ}}{C_c}\right) e^{-t/\tau_s} + \frac{C_f}{C_c}\,\frac{1}{(1+\tau_1/\tau_2)}\,\frac{\mathrm{Sin}(\omega t+\delta)}{1+\omega^2\tau^2} \qquad (8\text{-}3)$$

The concentration of reacted pollutants in the contents easily can be calculated from this equation, but was not done since it would add no new insight.

Appendix A-9

Empty Container With Reactive Walls: Exact Solution

In this model we consider an empty container, but the walls are of material that can react with the pollutant by a first order reaction as the pollutant diffuses through them. All problems of combined diffusion and reaction are difficult, and the exact solution is sketched out because it appears not to exist in the literature and because it is an important model.

For diffusion with first order reaction, the basic diffusion equation is

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2} - kc \qquad (9\text{-}1)$$

The boundary conditions are the same as in A-2, again assuming that C_1 does not vary with position thus

$$C(X,0) = C_o(X) \qquad (9\text{-}2)$$

$$C(0,t) = SC_1(t),\ C_1(0) = C_1{}^{\circ} \qquad (9\text{-}3)$$

$$C(\ell,t) = SC_2(t) \qquad (9\text{-}4)$$

$$\frac{\partial C_1}{\partial t} = \frac{AD}{V} \frac{\partial C}{\partial x}\bigg|_{x=o} \qquad (9\text{-}5)$$

Now define $C_e(X,t)$ by the equation

$$C = C_e\ e^{-kt} \qquad (9\text{-}6)$$

then Eqs. 9-1 to 9-5 become

$$\frac{\partial C_e}{\partial t} = D \frac{\partial^2 C_e}{\partial x^2} \qquad (9\text{-}7)$$

$$C_e(X,0) = C_o(X) \qquad (9\text{-}8)$$

$$C_e(o,t) = SC_1(t)e^{kt} \qquad (9\text{-}9)$$

$$C_e(\ell,t) = SC_2 e^{kt} \qquad (9\text{-}10)$$

$$\frac{\partial C_1}{\partial t} = \frac{AD}{V} e^{-kt} \frac{\partial C_e}{OX}\bigg|_{x=o} \qquad (9\text{-}11)$$

Eqs. 9-7 to 9-11 now form a boundary value problem with time dependent boundary conditions, and we use the same methods in solving it. A rather tedious algebraic manipulation leads to the following equation

$$\frac{V\ell}{ADS}\frac{\partial C_1}{\partial t} = C_2 - C_1(t) - 2\sum_1 Dne^{-\kappa t}$$

$$+ 2\sum_1 \frac{kC_2(-)^n}{\kappa}\left[1 - e^{-\kappa t}\right]$$

$$- 2\sum\int \left[C_1'(\tau)+kC_1(\tau)\right] \exp\left[-\kappa(t-\tau)\right] d\tau \qquad (9\text{-}12)$$

where

$$\kappa = \frac{D_n{}^2\pi^2}{\ell^2} + k \qquad (9\text{-}13)$$

$$D_n = C_1{}^\circ - (-)^n C_2 - \frac{n\pi}{2} C_n \qquad (9\text{-}14)$$

$$C_n = \frac{2}{\ell}\int_0^\ell C_o(x)\ \mathrm{Sin}\ \frac{n\pi x}{\ell}\ d\ell \qquad (9\text{-}15)$$

And all the other quantities have the same meaning as previously.

Eq. 9-12 is an integro-differential equation for C_1, and is the analogue of Eq. 2-14. Indeed, it will be seen that the former reduces to the latter as $\kappa\to o$, as it must. However, it is not clear that the methods used in A-2 will solve Eq. 9-12. Machine methods might be used, but the matter was not pursued as being too detailed for the purposes of this study.

Appendix A-10

Container With Reactive Walls: Steady State Solution

A. Introduction

Because reaction as well as diffusion is taking place in the walls, it was felt that it would not be realistic to assume a linear concentration gradient in the walls. Then, since the exact solution given in A-9 is far too complex to use, the only approximate solution that can be obtained is at steady state. This occurs a long time after the container has been sealed, after all the transients solved for in previous Appendices have died out. This is obviously a limited approach, but fortunately gives considerable insight. In this model, the exterior concentration is assumed to be constant. First we consider an empty container, then one filled with reactive contents.

B. Empty Container

At steady state, the boundary value problem in A-9 reduces to the following

$$D \frac{\partial^2 C}{\partial x^2} - kC = 0 \qquad (10\text{-}1)$$

$$C(o) = SC_1 \qquad (10\text{-}2)$$

$$C(\ell) = SC_2 \qquad (10\text{-}3)$$

Eq. 10-1 is easily solved in terms of hyperbolic sines and cosines. The solution that satisfies Eqs. 10-2 and 10-3 is

$$C = C_1 S \operatorname{Cosh} rX + \frac{SC_2 - SC_1 \operatorname{Cosh} r\ell}{\operatorname{Sinh} r\ell} \operatorname{Sinh} rX \qquad (10\text{-}4)$$

where $r = (k/D)^{1/2}$

Note that this gives only the concentration profile in the walls of the container. That in itself is of little use. However, from it we can calculate the flux into the container from Fick's first law of diffusion:

$$F = D \frac{\partial C}{\partial x} \bigg|_{x=o} \tag{10-5}$$

Carrying this out gives

$$F = (Dk)^{1/2} \frac{SC_2 - C_1 S \text{ Cosh } r\ell)}{\text{Sinh } r\ell} \tag{10-6}$$

If the box is empty, i.e., with nothing in it to consume this flux, the flux must be zero. This gives the interesting result for the ratio of C_1/C_2 to be zero

$$C_1/C_2 = \frac{1}{\text{Cosh } r\ell} \tag{10-7}$$

An explanation of this result is given in the text.

C. Container with Reactive Contents

As already mentioned above, if the container is not empty, the flux of pollutant into the container must be consumed by the contents at just such a rate as to keep the concentration constant, as it must be at steady state. However, the rate of reaction depends upon C_1 so we must first find the value of C_1 at which the rate of reaction is just equal to the total flux.

To proceed, we must be careful of our constants. The reactivity of the contents need not be the same as the reactivity of the walls. Hence in what follows we let k_w be the reaction rate constant for the walls and k_c that for the constants. Now, as discussed in A-1, the total rate of reaction of pollutant with the contents is given by

$$V_c \frac{dC_r}{dt} = V_c k_c C_c = V_c k_c S C_1 \qquad (10\text{-}8)$$

Equating this to the total flux we obtain

$$V_c k_c S C_1 = A\ (Dk_w)^{1/2}\ \frac{(SC_2 - SC_1\ \mathrm{Cosh}\ r_w \ell)}{\mathrm{Sinh}\ r_w \ell} \qquad (10\text{-}9)$$

where $r_w = (k_w/D)^{1/2}$

Solving this for C_1 gives

$$C_1 = \frac{C_2}{\frac{Vc}{A} \frac{k_c}{\sqrt{Dk_w}}\ \mathrm{Sinh}\ r_w \ell + \mathrm{Cosh}\ r_w \ell} \qquad (10\text{-}10)$$

Now having the steady state value of C_1, we can calculate the rate of increase of reacted pollutant in the contents simply by multiplying this by $k_c S$. Without a container, the rate would be simply kSC_2.

Appendix A-11

Sorption in a Sheet with Reaction

For this model, imagine a sheet of thickness 2ℓ immersed in an atmosphere containing pollutant. Pollutant diffuses into the sheet and reacts with it. This is the model described in A-9 and A-10, but with $C_1 = C_2$. Because the time-dependent solution is too complex to be useful, only the steady state solution will be given. This problem has been solved by Odian & Kruse (18). Note that at steady state, the concentration profile of unreacted pollution does not change, but the concentration of <u>reacted</u> pollutant increases steadily.

Following A-10, assume the sheet thickness extends from $-\ell$ to $+\ell$, so that its thickness in now 2ℓ. The boundary value problem now becomes

$$D \frac{\partial^2 C}{\partial x^2} - kC = 0 \qquad (11\text{-}1)$$

$$C(\ell) = C(-\ell) = C_g \qquad (11\text{-}2)$$

where C_g is the surface concentration, the solution to this is

$$C(x) = \frac{C_g \text{ Cosh } rx}{\text{Cosh } r\ell} \qquad (11\text{-}3)$$

where $r = (k/D)^{1/2}$

The average concentration of unreacted pollutant is

$$\bar{C} = \frac{1}{2\ell} \int_{-\ell}^{\ell} C(x)\, dx \qquad (11\text{-}4)$$

which yields

$$\bar{C} = \frac{C_g}{\ell} \quad \frac{\tanh r\ell}{r} \qquad (11\text{-}5)$$

Since the rate of increase of the concentration of reacted pollutants is $k\,\bar{C}$, the slope m of the curve of reacted pollutant concentration vs time is

$$m = \frac{C_s k}{\ell} \; \frac{\tanh r\ell}{r} \tag{11-6}$$

This may be cast in the more convenient form for solution by iteration

$$\frac{m}{C_s} \; \frac{\ell}{\sqrt{D}} \; \frac{1}{\sqrt{k}} = \tanh \; \sqrt{k} \, \frac{\ell}{\sqrt{D}} \tag{11-7}$$

ADDENDUM

ADDENDUM

Temperature and Water Vapor Microenvironments

A.1 Introduction

With good temperature and relative humidity control in the archive stacks, these microenvironments are not expected to be greatly different from the macroenvironment. However, for the sake of completeness, temperature and water vapor microenvironments are discussed in this Addendum.

A.2 The Temperature Microenvironment

The temperature microenvironment is important because the rate of degradation reactions generally varies with temperature, specifically according to the Arrhenius law. As the temperature of the stacks varies, so will the temperature inside a container filled with documents, or in the interior of a book. As is readily apparent, however, the temperature in the interior will lag that in the exterior, and, if the exterior temperature cycles with a given excursion, the interior temperature will cycle with a smaller excursion, whose magnitude, however, will depend on the position in the book or container. At the very edge of the book or container, the temperature will be the same as the exterior temperature. At the center of the book or container, the temperature variation may be only a small fraction of the exterior variation, depending on the period of the cycling, the size of the book or container, and the thermal conductivity, or more precisely, the thermal diffusivity, which is the ratio of the thermal conductivity to the product of specific heat and density. The only question that arises is the magnitude of the effect.

To illustrate this, we have made calculations for three specific cases: an isolated book; a document box; and a row of books tightly packed on a bookshelf. In each case it is assumed that initially the temperature in each of these three items is uniform. At a given time, the exterior temperature is changed by a given number of degrees. We ask, "What is the temperature as a function of time and position inside the item in question?"

To solve this problem we need to know the values of thermal conductivity, specific heat, and density for the material in the book, document box, and shelf of books. First, consider the book. Except for the cover, the book may be considered to be a solid block of paper. Now, the American Institute of Physics Handbook (1) gives the thermal conductivity of rice paper and blotting paper as 0.00011 and 0.00015 cal/cm^2/K/sec respectively. The specific heat of most cellulose-like polymers is approximately 0.3cal/gmK, and we have taken the density to be unity. More accurate values are not necessary for our semi-quantitative purposes. Hence we obtain the value of 0.0004cm^2/sec for the thermal diffusivity. We have also assumed that the book covers have the same diffusivity, which is reasonable for our purposes.

The situation for the document box is somewhat different. Here there is an air space. The thermal conductivity of air is quite low, being about half that of the paper given above. However, the thermal diffusivity is very high because of the low specific heat and density. To solve the container problem exactly becomes one of the Models Not Solved in Sec. 2.10. We have instead done a simpler problem and assumed that the container is tightly packed with documents, ignoring the air space.

Each of these problems then becomes that of calculating the temperature as a function of position and time in a rectangular parallelipiped which was originally at a uniform temperature and is suddenly placed in an environment at a different temperature. This is a standard problem in Fourier series whose solution is given in standard texts (3,4). This solution was used to calculate the temperature-time-position curves in Figs. A-1 to A-3. Obviously, there is an infinity of positions that could that be chosen, but only a few were, as discussed for each separate set of curves.

Fig. A-1 is for an isolated book. Its dimensions are 5cmx16.5cmx24.8cm. The positions chosen area at the center of the book, and along the 5cm dimension at the midpoint of the other dimensions. The results are given as $(T-T_e)/(T_0-T_e)$, where T_e is the exterior temperature and T_0 is the original uniform temperature. Clearly, the curves can be scaled for any temperature difference (T_0-T_e) by simply multiplying the ordinate by this value. Curves are given for 10min,. 40min, 1hr, and 4hrs. Also indicated by the dashed line is the temperature distribution at zero time, i.e., the time at which the external temperature was suddenly changed. After nine hours (not shown) the whole book is essentially at the temperature of the exterior. As expected, the center of the book is the slowest to change, and the surface regions change most rapidly. This will become more apparent in subsequent figures.

Figure A-2 is the analogue of Fig. A-1, but for the prototypical container tightly packed with documents. This again is treated as rectangular parallelipiped. The dimensions are 12cmx26cmx38cm, and again the temperatures are along the short dimension along the center line of the container. Here curves are given for 1,4, 9, 16 and 25 hrs. As compared with Fig. A-1, changes are much slower in the interior of the container, due, of course, to the greater thickness. Here, after one hour, approximately 60% of this region of the container has changed in temperature by less than 10% of the temperature change, while the remainder has changed by an average of about 50%.

Finally, in Fig. A-3 we show what happens when books are tightly packed on a shelf. Here the shelf is 85cm long (the dimension of a bookshelf in the Polymers Division Library), and the lateral dimensions of the books were taken to be 16.5cmx24.8cm. Temperatures were calculated along the 16.5cm dimension at the mid-point of the book stack. It was to be expected that the temperature changes in this case would the slowest of the three cases studied, and this is borne out as shown in Fig. A-3. Here, after one hour, in this region of the stack of books, a full 50% of the book has shown essentially no temperature change, and about 75% has shown and average temperature change of less than one degree.

It is clear from physical reasoning and could easily be shown by more extensive calculations that the faces, edges and corners of books, stacks of books, and document boxes follow temperature excursions more closely than the interiors of these items. The interior is "shielded" from changes occurring in the exterior. It seems reasonably clear that, given regular changes is the exterior, at steady state the center of the item will be at the average temperature with small changes that mimic the exterior, while the surface regions will follow the exterior changes, but less and less closely depending on the depth.

What use is to be made of these data? Clearly, what we are interested in is not the temperature per se, but the extent of reaction. We therefore now consider how this information on temperature as a function of time and position can be used to calculate the extent of reaction also as a function of time and position. For the sake of illustration, assume we are interested in a property such as specific absorption coefficient, A. Other properties could be used; all that is required is that the rate law be known. Then, as shown by Browning and Wink (5), A varies with time as follows:

$$dA/dt = k \qquad \text{(A1)}$$

The rate constant k is a function of temperature and follows the Arrhenius law, which we may write as follows:

$$k = k_0 \exp[-\Delta H/RT] \qquad \text{(A2)}$$

Now, the temperature is a function of position, x,y,z, and time, t, and therefore so also will be the rate constant, as follows:

$$k = k_0 \exp[-\Delta H/RT(x,y,z;t)] \qquad \text{(A3)}$$

Hence, at any point x,y,z we can write

$$dA(x,y,z;t)/dt = k_0 \exp[-\Delta H/RT(x,y,z;t)] \qquad \text{(A4)}$$

Finally, for the change in the A at a point x,y,z after exposure to a temperature T for a time t, we obtain the following

$$A(x,y,z;t) - A_0 = k_0 \int_0^t \exp[-\Delta H/RT(x,y,z;t])dt \qquad \text{(A5)}$$

where A_0 is the specific absorption coefficient at zero time. What this equation shows is that knowing the temperature as a function of time and position, the change in A can be calculated as a function of time and position by carrying out the integration, which would generally have to be done numerically. If, for example, the temperature around a book were suddenly increased by say 10 degrees, then curves like those in Fig. A-1, but for all points of interest in the book, could be used to calculate the change in A at those points. It is, of course, necessary to know the activation energy and the coefficient k_0, but these are available for many of the properties of interest, or could be measured. Again, this could be done for other properties of interest, provided only that the rate law is known, as well as the change with temperature of the rate constant. Average values of the change in property are also easily calculated, but it is felt here that this is not a very useful quantity.

With this in mind, and with the data in the figures, what can be said in a general way about the difference in the rate of reaction between the surface regions and the interior central regions of the book? Consider the following idealized situation. A book is placed in an environment in which the temperature fluctuates in a regular, systematic manner. Half the time the temperature is $T_0+\Delta T$ and half the time it is $T_0-\Delta T$. The average temperature is then T_0. Further to simplify the problem and the reasoning, assume that steady state has been reached, and that the book is big enough, or the cycle time short enough, that the center of the book is essentially always at the average temperature. Now consider a given degradation reaction. At the center of the book, the reaction will proceed at a constant rate. In the surface regions of the book, and particularly at the edges and corners of the pages, the situation is quite different. Here the temperature follows the ambient temperature, the more closely the nearer the location is to the very surface of the book. On the high temperature part of the cycle, the reaction will occur more rapidly than in the interior, while on the low temperature part the reaction will occur less rapidly than in the interior. However, because of the exponential Arrhenius dependence of the rate constant on temperature, the net effect is that the extent of reaction in the surface regions will always be greater than in the center portion of the book. While this can be shown analytically, it can also be reasoned in the following manner. Suppose the reaction rate constant at $T_0+\Delta T$ is just twice what it is at T_0. (For an activation energy of 30kCal, as for specific absorption (5), ΔT is 4.16K.). And consider one cycle of the temperature scheme outlined above. Then, the center portion of the book spends the full cycle at the temperature T_0, and the surface spends 1/2 cycle at $T_0+\Delta T$ and 1/2 cycle at $T_0-\Delta T$. However, in the 1/2 cycle at $T_0+\Delta T$, as much reaction occurs as in one full cycle at T_0. In addition, at $T_0-\Delta T$, reaction still proceeds, albeit at a reduced rate of about 1/2 that at T_0. The amount of reaction that occurs at this lower temperature is the added extent of reaction that occurs at the surface of the book as compared to the center. Thus, the extent of reaction at the surface of the book is greater than in the center. Actual calculations for $T_0=298K$, $\Delta T=4.16$, with an activation energy of 30kCal show, in relative units, the extent of reaction in the interior is 1.38, while at the edges of the pages, which follow the ambient temperature, the extent of reaction is 1.72.

How much this effect has to do with the yellow discoloration borders on the edges of book pages is not known, but it could very well be a contributing factor. As discussed in the main body of the report, diffusion of pollutant into the book is also very likely a contributing factor, and it is to be noted that the temperature and pollutant act synergistically.

A.2.1 Conclusions

1. In books or document boxes, the variation in temperature as the exterior temperature varies is greater in the surface regions than in the central regions of the item. Knowing the dimensions and the thermal diffusivity of the item, the variation of temperature with time at any position in the item can be calculated, at least approximately.

2. The measurement of temperatures in an item like a book or document box following a sudden change in the exterior temperature are easy measurements to make and would be instructive.

3. Because of the Arrhenius dependence of rate constants on temperature, in a fluctuating temperature environment the extent of reaction in the surface regions of books and document boxes will be greater than in the central regions of the item.

A.3 The Water Vapor Microenvironment

The water vapor microenvironment, usually characterized by the relative humidity, is important because it determines the moisture content of the records. This latter is an important quantity, particularly with paper, because, as discussed in the main text, one of the principal degradation reactions of paper is hydrolysis, the rate of which is proportional to the moisture concentration, and at the higher moisture contents, microorganisms can grow (6). It is thus important to analyze the water vapor microenvironment as was done in the main text for pollutants. Indeed, the same techniques can be used for water vapor as for pollutants, but with some added qualifications, as will be discussed in what follows.

First, it is important to recognize that, for pollutants, the principal function of a container was to keep pollutants out. This could be done with a sealed, impermeable container (which led to complications, as discussed in the text), or with one that reacted with the pollutants and thus acted as a "scavenger". With water vapor, shielding of the contents by impermeable containers might not be practical, because of the initial conditions. If, for example, documents with a high moisture content were sealed in an impermeable container, then the moisture content would remain sensibly constant, their rate of degradation would be relatively high, and they might be subject to microorganisms. Hence, with water vapor, it would be better to provide water vapor access between the interior of the container and the exterior, assuming a reasonable control of the exterior Rh.

The analysis of the transport of water vapor between the interior and exterior of a container follows the same analysis as was used for pollutants. In this case, however, no reaction is considered in either the contents or the walls of the container. The reason is that paper at normal Rh contains such a large amount of water that its concentration will not be changed a great deal as hydrolysis takes place. (Note that at 4% regain, the mole fraction of water in cellulose, based on cellulose monomers, is 0.27, and that a change in the degree of polymerization involves only a very few hydrolytic attacks per cellulose molecule.) Now, in the analysis of microenvironments with pollutants, a relaxation time was developed. Its magnitude was given by $V\ell/ADS$, where V is the total volume of the container (including the volume at STP of the pollutant in solution in the contents), ℓ is the thickness of the container walls, A their area, D their diffusion constant, and S the solubility of pollutant in them as defined in Appendix A-1. This quantity is a measure of the time necessary for the interior and exterior of a container to come to equilibrium following a sudden change in the conditions in one of them. The same analysis as for pollutants applies to water vapor, and in what follows we will principally discuss the value of this relaxation time for water vapor, comparing its value to those developed for pollutants.

There are two material constants in the relaxation time: D and S. They will vary with the material of the container wall and with the gas or vapor. We will discuss S, the solubility parameter first.

The quantity S, as defined in Appendix A-1, is the concentration in $cm^3(STP)/cm^3$ in the solid phase divided by the mole fraction in the gas phase, all at one atmosphere pressure. For the cellulose-water vapor system, this quantity is not a constant, because the regain curve is not linear over its whole range. Direct calculations from the data of Jeffries for unbleached spruce sulfite pulp (7) show that S varies from 11,200 at 5% Rh to 3780 at 80% Rh. However, in the region from 30% to 70% Rh, the regain curve is quite linear, and S varies from 4340 to 3650. Hence, as an approximation, we may take S to be 4000 in this Rh range. The magnitude of this quantity will be discussed below.

In contrast to cellulose, polyethylene (PE) and polypropylene (PP) have values of S of 2.5 and 2.9, respectively (8). This is totally in accord with expectation; water is essentially insoluble in the two polyolefin polymers, but quite soluble in the anhydroglucose polymer.

The other material property we need is the diffusion constant, D. For PE and PP, these are known, and are the high values of 230×10^{-9} and 240×10^{-9} cm^2/sec, respectively. For cellulose in the form of paper, we have been unable to find any data on diffusion constant for water. There are, however, data on regenerated cellulose. The most complete study was done by Newns(9), who determined values for D of less than 10^{-9} at low moisture contents, to values greater than 10^{-8} at high moisture contents, higher than those normally found in paper. How paper would compare to this is unknown. Considering that paper is a looser structure than regenerated cellulose, and purely for purposes of illustration, we have chosen a value of 10^{-8} cm^2/sec. This could be in considerable error. Then, it is to be noted that only the product DS appears in the expression for τ. All these data have been collected in Table A-1, where there are also listed the values for SO_2 used previously.

While the data for PE an PP are fairly sound, the data for paper, except for S, are undoubtedly not quantitatively correct. Nevertheless, the qualitative trend is in accord with expectation. First note the values for S. As previously mentioned, these indicate that S for water vapor in paper is more than 1000 times as great as it is for water in PE or PP. Also note that S for water vapor in paper is more than 100 times as great as for SO_2 in paper. These are probably fairly well established and are in accord with expectations. The diffusion constants in paper have already been discussed and are not well established, but those for PE and PP are actual literature values (8). The uncertainty in the values of DS then stems largely from the uncertainty in the values of D for paper. This is as expected, since this is the hardest quantity to determine.

We now discuss the significance of these results. Recall that the product DS enters into the denominator of the expression for the relaxation time. Hence, from this factor alone, an increase in this means a shortening of the relaxation time. Thus, comparing empty paperboard containers without gaps for water and SO_2, it is seen that with water vapor the interior of the container comes into equilibrium with the exterior 100 to 1000 times as rapidly as it does for SO_2. Similarly, for empty containers and water vapor, the paperboard container comes into equilibrium nearly 1000 times as fast as similar containers made of PE or PP. Because of the uncertainties in the diffusion constant, as previously discussed, the quantitative values may be incorrect, but the trend is certainly correct.

If, however the container contains paper documents, even loosely packed so that equilibrium between them and the interior environment of the container always obtains, the situation is quite different. This is because of the volume V in the numerator of the expression for the relaxation time. Recall that this V was the empty volume plus the volume of gas or vapor in solution in the contents (See Appendix A-1). Now, assuming a reasonable quantity of paper documents in the container (of the order of half full), the volume of water vapor in the contents far exceeds the unoccupied volume in the container. In this case, $V \approx SV_c$, where V_c is the volume of the contents. Now consider the paperboard container. Here we may safely assume that S is the same for the contents as for the walls. In this case, the relaxation time is independent of S, and, compared to the empty container, is approximately S times as great (4000 for our specific example). Now consider the case of the container with polyolefin walls. Here again the relaxation times compared to the empty container increase by a factor of the value of S for the contents. In effect, the high solubility of water vapor in the container contents increases the volume of the container several thousand fold, and that much more water vapor must diffuse through the walls to obtain equilibrium. This water vapor stabilizing effect of paper is well known, and was used in the design of the Constitution and Declaration of Independence cases, which contain a thick layer of pure α cellulose.

A.3.1

1) Because the initial moisture content of documents to be boxed is not necessarily controlled, impermeable containers are not practical for controlling moisture content.

2) The high solubility of water vapor in cellulose dramatically lowers the rate at which the interior of a box filled with cellulosic documents comes into equilibrium with the external environment as compared to an empty box.

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TABLE A-1

Solubility and Diffusion Constant for Water Vapor

Material	S	D, cm^2/sec, $x10^9$	DS, cm^2/sec, $x10^7$
Paper	4000	10[a]	400
PE	2.5	230	5.8
pp	2.9	240	7
Paper(SO_2)	30	1-10	0.3-3

[a] Little more than a guess

ADDENDUM FIGURE CAPTIONS

Fig. A-1 Reduced temperature at various locations along the shortest dimension of a book at various times after a sudden change in the external temperature. To obtain the actual temperature change, the ordinate should be multiplied by the magnitude of the sudden temperature change.

Fig. A-2 Same as Fig. A-1 but for a completely filled document box of the same dimensions as the prototypical container.

Fig. A-3. Samer as Fig. A-1 but for a shelf of books. The locations are at the center of the stack of books along the shortest dimension.

Fig. A1

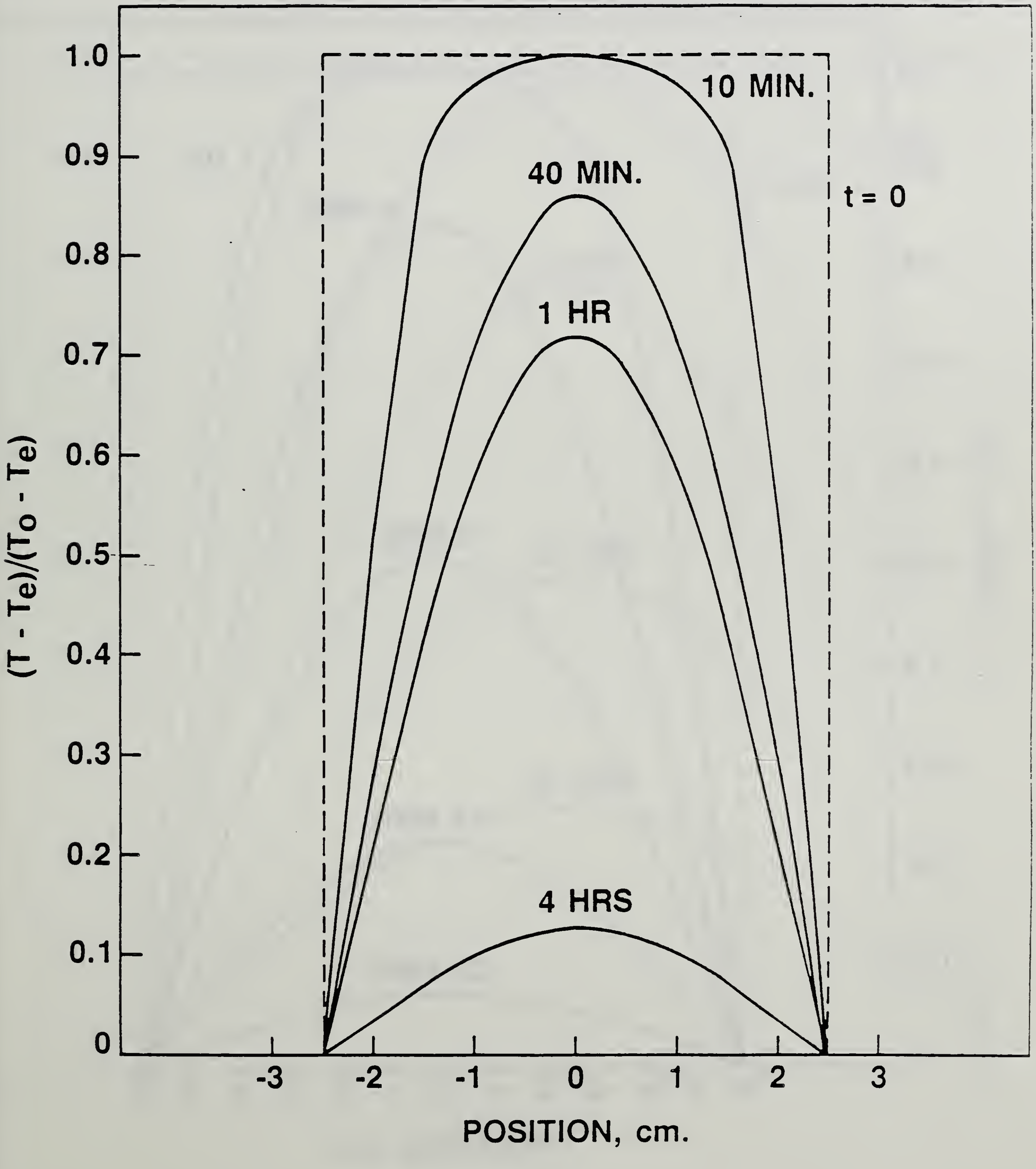

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
(T - Te)/(To - Te)
10 MIN.
40 MIN.
1 HR
4 HRS
t = 0
-3
-2
-1
0
1
2
3
POSITION, cm.

Fig. A2

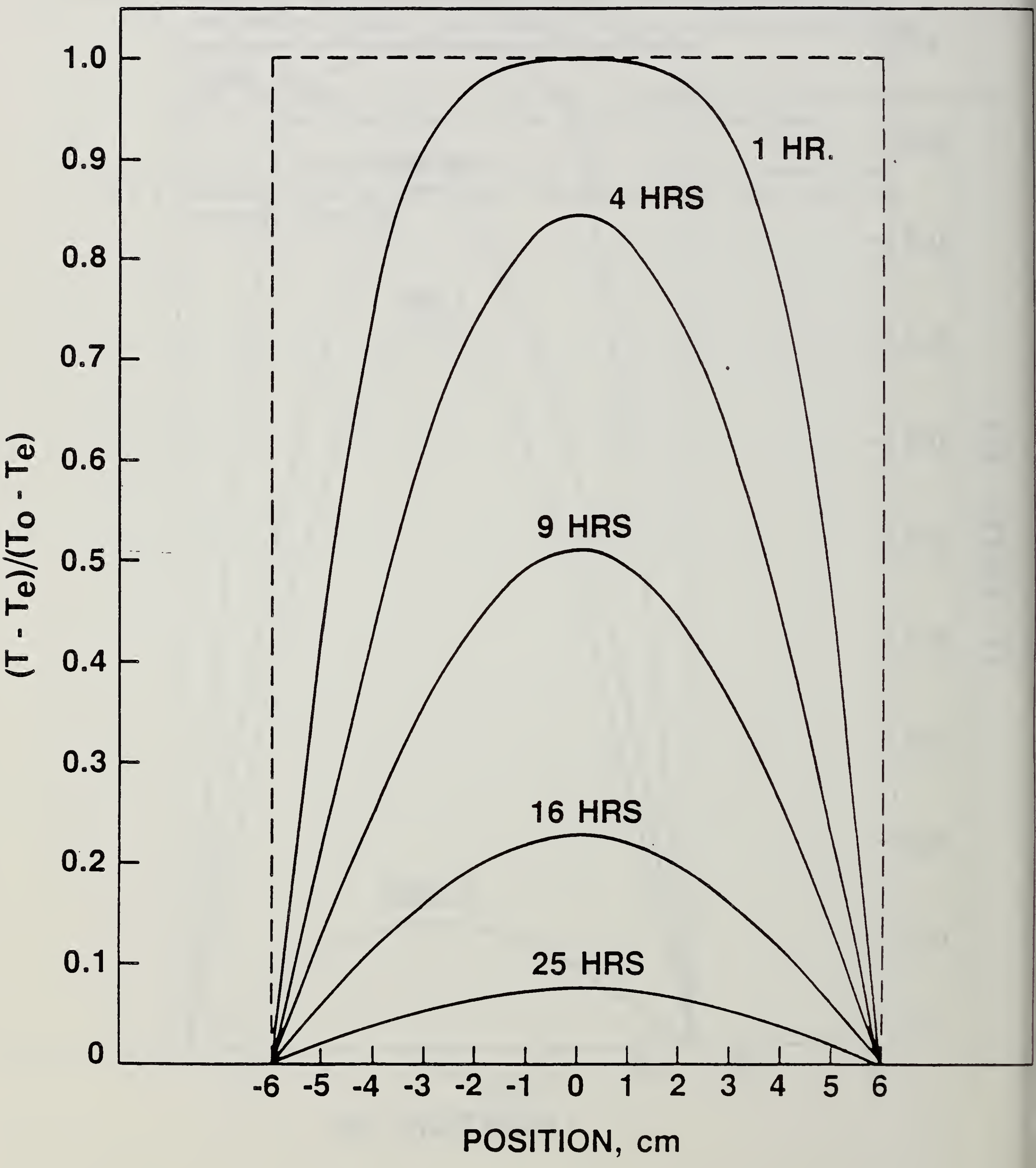
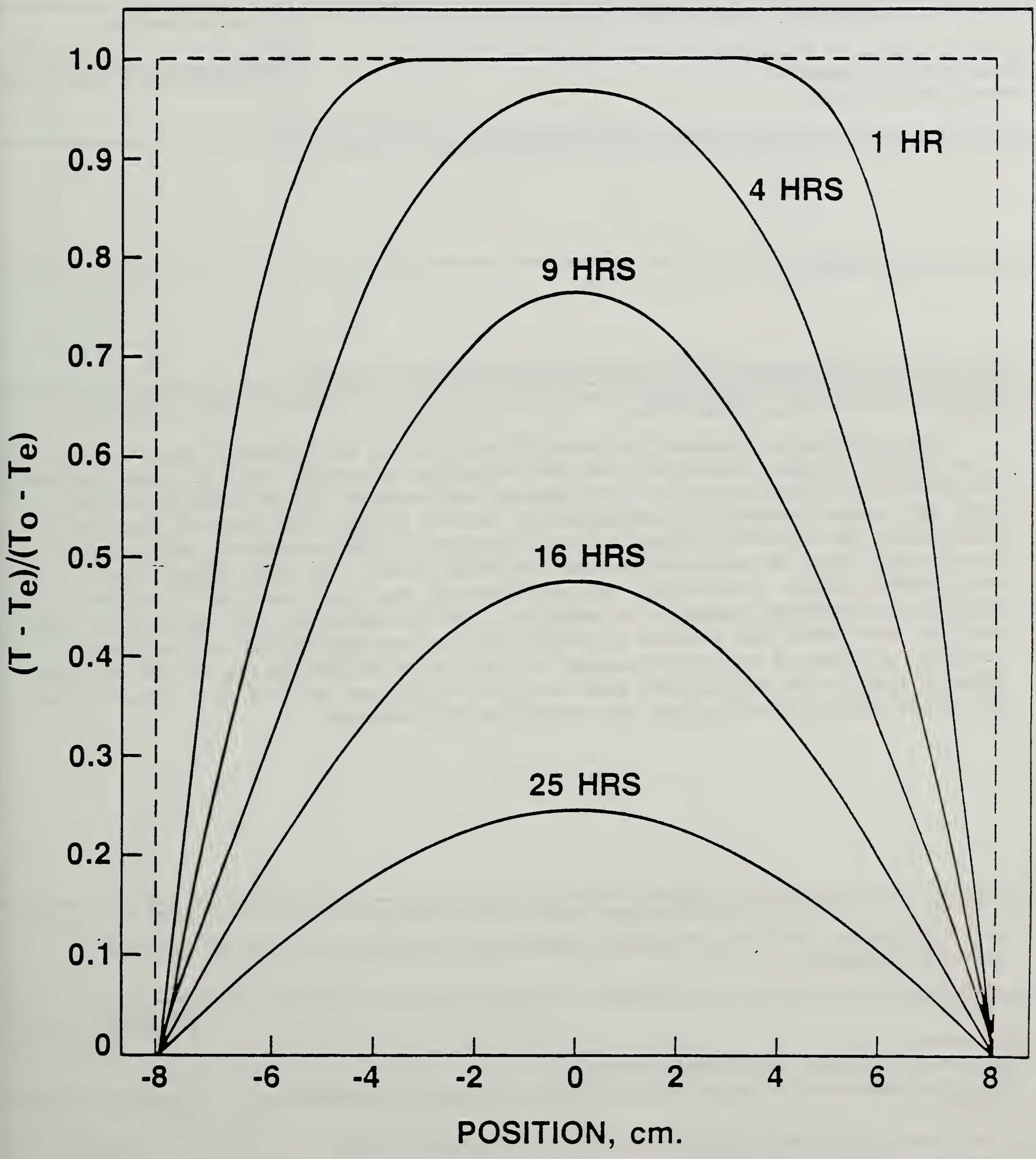

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
(T - Te)/(To - Te)
1 HR.
4 HRS
9 HRS
16 HRS
25 HRS
-6
-5
-4
-3
-2
-1
0
1
2
3
4
5
6
POSITION, cm

Fig. A3



1 HR
4 HRS
9 HRS
16 HRS
25 HRS
(T - Te)/(To - Te)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-8
-6
-4
-2
0
2
4
6
8
POSITION, cm.

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U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO. NBSIR 87-3635	2. Performing Organ. Report No.	3. Publication Date

4. TITLE AND SUBTITLE

The Characterization of Microenvironments and the Degradation of Archival Records: A Research Program

5. AUTHOR(S)

Elio Passaglia

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
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8. Type of Report & Period Covered

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Air pollutants increase the rate of degradation of documents and records in archival storage. However, with the exception of books, most of these documents and records are not exposed to the ambient environment of the archive stacks. They are instead stored in containers of various kinds. The records therefore experience the microenvironment of the interior of the container, which may be more benign than the macroenvironment exterior to it. In this report, the environment inside a container, and any changes that can occur in it as the exterior environment changes, is modelled. On the basis of this modelling, and what is know about the effects of pollutants on the degradation of archival records, a research program designed to lead to an understanding of the maximum benefit that could be obtained with various containers is laid out. The design and materials of construction are specifically discussed.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Air pollutants; archival records; degradation; diffusion; lifetime testing; microenvironments.

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14. NO. OF PRINTED PAGES
127

15. Price
$18.95