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The Development of Guidance for Solving Polymer-Penetrant Diffusion Problems in Marine Hardware

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THE DEVELOPMENT OF GUIDANCE FOR SOLVING

POLYMER-PENETRANT DIFFUSION PROBLEMS

IN MARINE HARDWARE

BY

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ABSTRACT

There is a need for the development and trial of an accessible, robust procedure that can be followed to solve polymer-penetrant diffusion problems associated with marine hardware failures, incorporating some of the complexities abounding in these types of systems. The goals of this guidance are to instruct design engineers in the appropriate methods to apply when predicting diffusion phenomena as well as to assist them when selecting materials for diffusion-susceptible or -dependent applications, especially those related to marine hardware. A straightforward step-by-step flowchart tool is presented to accomplish this instruction to average scientists and engineers not deeply versed in the specifics of polymer-penetrant diffusion. The tool is based on fundamentals of mass transport from literature and is broken into 3 large steps: 1, forming the problem; 2, identifying the math; 3, applying the solution method. Auxiliary relevant resources for quantitative solution of the diffusion problems are compiled and presented to help users find tabulated values of coefficients and parameters from the resulting solution equations. The development of the flowchart tool and worked-through diffusion problem examples are presented to demonstrate its origin, use, and the scope of the effort required in order to develop solutions for mass transfer problems. Polymer barrier properties can be improved through the addition of nanoclay platelet fillers; this subject is presented in some detail to illustrate complexities of real-world transport problems and connect their origins to the fundamental steps of the flowchart tool developed herein.

ACKNOWLEDGEMENTS

DEDICATION

To my family,

"...those who are here,
those who are not here,
those who have gone from here,
and those who are yet to come."
– Theodore Mayer

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CHAPTER 1: INTRODUCTION

The problem I am trying to solve:

Diffusion describes the dispersion of chemical in a system from areas of high concentration to lower concentration due to random-walk molecular motions of the particles. This fundamental phenomenon is modeled differently when it occurs in gases, liquids, solids, and polymers (1).

There is a need for the development and trial of an accessible, robust procedure that can be followed to solve polymer-penetrant diffusion problems associated with marine hardware failures, incorporating some of the complexities abounding in these types of systems.

The goals of this guidance are to instruct design engineers in the appropriate methods to apply when confronted with two fundamental questions related to diffusive mass transfer in marine hardware coatings and components:

A. How long until X occurs? 'X' can be the concentration or flux of a chemical species at a certain location in the hardware reaching a specific level of interest.

B. What material should I select for my application to avoid diffusive-mass-transfer-related issues?

Question A may be encountered when dealing with an existing system that may be experiencing a problem, or to assess risk for a potential problem in an existing system. It may also be an important question to answer when finding a solution to question B. Many performance requirements are made of materials used in marine hardware systems besides those related to diffusive mass transfer (e.g. structural strength, acoustics, corrosion resistance), and may dominate the material selection

decision of a design engineer. It has been my experience that reliance on materials of historical familiarity is sometimes used as a surrogate to understanding complex phenomena, even if the modern application is different from the historical one.

Motivating examples from work experience with marine hardware:

The origin of this thesis topic comes from my experience working at the Naval Undersea Warfare Center (NUWC) in Newport, RI. Problems within the scope of polymer-penetrant diffusion I encountered in over 6 years of employment still remain current topics of interest. During their investigation, I found I had an insufficient understanding of the fundamentals of the problem and a lack of guidance from insufficient corporate knowledge in the subject. Future needs of a similar nature are anticipated, prompting my choice of subject area for advanced education. A few examples follow of problems I have encountered which illustrate the challenges motivating my choice of thesis topic.

Working in the Devices, Sensors, and Materials Research and Development branch of the Sensors and Sonar Systems department has led to my involvement in a number of failure analysis investigations of marine hardware systems. In two such cases, the diffusion of water through multiple layers of different materials led to an electrical failure of the internal hardware. In one case a proposed dip-coating fix was revealed to be insufficient as the diffusion coefficient of water through the dip-coating was too high for it to be an effective barrier. This was shown by analogy in a brute-force experiment instead of by predictive modeling due to my insufficient knowledge to completely describe the phenomena. In the other investigation the measurement of diffusion coefficient by the gravimetric mass uptake method was confounded by

runaway water absorption forming entrained liquid blisters in the samples. Again, my lack of sufficient knowledge led to the inability to address the unexpected behavior and hampered diffusion coefficient calculation.

I believe good engineering design practice for material selection could be used to reduce the occurrence of these types of delayed problems. Through my involvement in the design end of marine hardware I found a lack of such reasonable guidance for material selection which incorporates diffusion behavior and other deleterious chemical interaction. Non-scientific accelerated water bath testing or vague 'compatibility' statements are often the only guidance offered to engineers that address these types of potential problems. These methods are presented as a 'one-size-fits-all' approach, but their results are highly dependent on sample materials, geometries, and temperature response of material property. In addition, the 'acceptable' numbers resulting from such tests reflect the common materials of the time; it is with great peril that one should apply such non-specific evaluation methods to the exotic and novel materials considered for the advanced hardware design of the future.

One application that is dependent upon polymer-penetrant diffusion is the use of environmentally acceptable biocides to prevent marine biofouling on flexible surfaces not accommodating to the typical painted-on anti-fouling solution. Marine biofouling causes noise and drag to a marine vessel (2), and can interfere with the proper operation of sensor arrays. In this case, the biocide is incorporated into the flexible coating material and protects the surface by slowly leaching out over time, discouraging marine organisms from landing and attaching. The success of this mechanism involves the diffusion of the biocide (penetrant) through the coating (polymer) until it can no

longer support the minimum release of biocide from the surface necessary to prevent fouling. The time to reach this minimum is a critical design parameter and is dependent upon the material properties of the biocide and coating, the geometry (thickness) of the coating, the degree of loading of biocide in the coating, and the ocean environment the surface is exposed to. A model is needed that considers these parameters and that can predict the efficacy of a biocide-laden coating solution.

To summarize my motivations, I am finding I need to solve polymer-penetrant diffusion problems, but they are occurring in different systems which have their own unique modeling challenges. Examples include the aforementioned biocide efficacy question, material selection for new design, accelerated life testing prediction, failure analysis, and diffusion measurement. Each system may be unique enough that it has its own field of advanced study. Do I have to be an expert in each field in order to solve the diversity of problems I encounter? No! That would take many lifetimes. Instead, I want to use the basic functional components of each of them in order to solve the majority of problems I encounter. More advanced problems would then require collaboration, the necessary resources for which will have already been conveniently compiled in this work. Diffusion is anticipated to be important for future navy systems that incorporate novel and exotic composite materials and additives. Polymers, plasticizers, and leachable components will all be subject to the persistence of random molecular motion, much more so than the ceramic and metallic materials of historic familiarity.

At the end of the day, I am most interested in improving the reliability of marine hardware systems, accurately predicting and extending their service life, and reducing

maintenance costs especially those associated with marine biofouling. I also hope to contribute innovative solutions to the incorporation of polymers in new applications and to improve quality control and specification to ensure the U.S. Navy is procuring appropriate materials in its systems. This would most likely manifest as scientifically valid, application-specific test requirements on procurements which rapidly and inexpensively check materials and components for problematic behaviors such as fluid incompatibility, permeation resistance, and incorrect formulation.

Difficulty with subject matter, lacking literature:

I have had difficulty in approaching these types of problems, and this lack of sufficient understanding partly motivated the choice of thesis topic. What seemed lacking in the literature was guidance akin to the TurboTax® tax preparation software concept, i.e. a user-friendly step-by-step approach which introduces the appropriate topics and asks for the right decisions along the way towards the ultimate solution. Human memory is naturally spatial (3) and works well with a flowchart since it represents a sequence of events as though along a path. Solving mass transport problems requires applying concepts of mass balance, constitutive relationships, differential equations, and evaluation of transcendental functions <u>in their proper order</u>. Getting the order of operations correct may seem straightforward to an experienced practitioner, however I can attest that it is confusing and frustrating for the novice. One particularly vexing trap is to stray too far from the original problem at hand while delving into the nuance of applying one of the aforementioned concepts, a sort of 'Hansel and Gretel' bewilderment as the breadcrumbs of our thought process fall prey to the complex gingerbread diorama challenge of incorporating new knowledge. The

added concept of mole-based or mass-based units leads to mass transport requiring at least twice the generic symbols and equations to handle the permutations of scenarios as compared to heat and momentum transport. Mathematical analogy is made in the literature between heat conduction and mass diffusion (4) (5), however mass diffusion has unique nuances which don't appear in heat transfer such as chemical reaction (1) and an apparent discontinuous concentration driving force between phases at equilibrium (although chemical potential is continuous, but practical transport phenomena equations presented in the literature avoid using chemical potential).

It is clear that much work has been done related to polymer and penetrant diffusion in the last 60 years and advancements continue today. In spite of all this effort, the incorporation of these diverse behaviors into the solution of real-world applications is not straightforward in the literature. Beyond the negation of simplifying assumptions, the hapless engineer is sent down an unfamiliar path delving deeply into the particular science of a unique behavior, with guidance returning the user to the original problem at hand noticeably absent. No user-friendly process seems to exist to pursue (in general) the solution of diffusion problems involving penetrants in polymers; no one resource has combined all tools necessary to approach the diversity of behaviors potentially encountered. Indeed, how does one navigate the dense jungle of polymer-penetrant diffusion knowledge between the polymer-penetrant diffusion problem and its solution? This thesis work offers to create that guidance to applying modern advances in the polymer-penetrant diffusion field to real-world problems, compiling the state-of-the-art and making it accessible to those not deeply involved in the basic research.

Complexity of the phenomena:

Many of the assumptions simplifying mass transport in gases and liquids do not apply to diffusion through polymers, as shown in the literature. In 1968, Fujita (6) notes that the sorption and permeation of organic vapors is "exceedingly complex" in polymers at temperatures below glass transition (T_g). Crank (5) highlights that the diffusion of vapors in high-polymers, different from most (e.g. dilute) systems, is concentration dependent, and a "very marked, characteristic feature" at that. Crank goes on to note a number of numerical solutions exist for these situations, however these solutions vary and are not uniformly applicable to all polymer-vapor systems. Vieth (7) concisely displays the potential for complexity when a condensable vapor (as opposed to a permanent gas) is diffusing through a rubbery polymer (above T_g); activation energy for diffusion (E_D), solubility, and diffusion coefficient can all be strong functions of penetrant concentration, more so if the temperature is near the polymer's T_g or if the penetrant acts as a plasticizer to the polymer. Stastna & De Kee (8) propose that "[g]enerally, the diffusion behavior of polymers cannot be described by Fick's law with constant boundary conditions." Neogi (9) affirms that, although the three assumptions of homogeneity, isotropy, and local equilibrium apply to conventional transport phenomena used to address fluids, "[n]one of these apply to solid polymers uniformly." Cussler (1) asserts that for low-molecular-weight solutes in a polymer solvent, diffusion modeling requires a blend of concepts from diffusion in solids and diffusion in liquids; I found it rather telling that this major work on diffusion phenomena purposefully omits a detailed discussion on diffusion in solids and restricts its scope to fluid systems. Finally, Kwan (10) summarizes many of these historically observed peculiar behaviors,

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stating that it is "…essential… to understand the nature of the diffusion of low molecular weight liquid penetrants into a given polymer matrix," and admits that after "several investigations" and "a variety of studies" there are now "various models" which describe the diffusion process.

One of the reasons for the complexity of these types of systems is the range of polymer and penetrant characteristics which can influence the diffusion process. The diffusion coefficient is nearly always temperature dependent, and may be concentration dependent (5). A very marked step-change in diffusion behavior generally occurs around the glass transition temperature of the polymer; over a narrow temperature range the types of accessible motions available to the polymer chain segments change significantly, impacting the mechanism of penetrant diffusion except for very small penetrant molecules, such as monatomic or diatomic gases. The relative time scales of polymer and penetrant molecular motion play a primary role in determining the type of diffusion which occurs in the system; Neogi (9) summarizes different power-law behavior of sorption data versus time in the expression

$$\frac{M_t}{M_\infty} = k_n t^\alpha$$

with α values reflecting the type of diffusion (e.g. pseudo-Fickian, classical/Fickian, anomalous, case II, super case II). Interaction or the lack thereof between polymer and penetrant molecules can lead to plasticization or penetrant clustering, respectively (7). Chemical reaction can also occur during the diffusion process, removing and generating chemical species with different diffusion behaviors (11) (12). Finally, diffusion through non-isotropic systems (e.g. inhomogeneous bulk material, composites, and layers) must

accommodate different diffusion behaviors in different phases and the transfer between them (1) (5).

How I am trying to solve the problem:

Specifically, the goal is to produce a straightforward step-by-step process flowchart tool for modeling the concentrations of small molecule penetrants (e.g. water, solvents, oils, plasticizers) within glassy and rubbery solid polymers as a function of position and time, making adjustments to include phenomena atypical to that found in the diffusion of gases and liquids.

This tool shall: be usable by the average scientist or engineer not deeply versed in the specifics of polymer-penetrant diffusion; provide guidance to the user to avoid mistakes, sanity check, and assess the expected range of accuracy of the prediction; be sufficient to address most types of polymer-penetrant diffusion problems; and be validated through experimental data both historical and novel.

Summary of the sections that follow:

Summary, Ch.2 Diffusion flowchart tool:

The key product of this thesis effort consists of a process flowchart tool which can be followed step-by-step to develop the equations and solutions of mass transport in solids, specifically polymers. The fundamentals of mass transport are reviewed from the literature, and the methods put forth by these authors form the basis of the flowchart process. The resulting flowchart process can be broadly described in three steps: 1, forming the problem; 2, identifying the math; 3, applying a solution method. Each step will be expanded upon in the detailed description of the tool. To facilitate use by the

target audience, general guidance and pitfall avoidance is also included to increase these users' chance of success.

Summary, Ch.3 Diffusion Resources:

This chapter summarizes the resources available for those seeking quantitative answers to their diffusion problem. It is intended as the 'next step' for users of the flowchart, enabling them to link values with the parameters developed in their solution equation. These tabulated values can come from various sources with a wide range of success, and include print literature, online databases, computer simulation, and experimentation.

Summary, Ch.4 Diffusion Problems:

This chapter highlights the work that influenced the development of the flowchart, and demonstrates its use through the solution of diffusion problem examples. Extensive math notes are included to convey the scope of the effort required in order to develop solutions for mass diffusion problems.

Summary, Ch.5 Barrier polymer application:

This section describes a method for dramatically reducing diffusion through a barrier polymer by adding nano-thick micron-sized clay platelets. Various models have been proposed to correlate the characteristics of the additive with the apparent diffusion. This section is included to illustrate complexities of real-world transport problems and connect their origins to the fundamental steps of the flowchart tool.

Future work / looking forward:

Current research in polymer-penetrant diffusion seems to focus in general on the need for computational solutions to the problem; good experimental techniques are

critical for end-use application, but the predictive power of computational methods is necessary given the vast number of experimental permutations of polymer-penetrant compound combinations. Bernardo et al.'s (13) review of polymer membrane separation technology emphasized the need for molecular dynamics studies and improved understanding of transport on a molecular level to advance the field, building on the computer simulation necessary to describe amorphous and semicrystalline polymers. Diffusion can be the determining factor of long-term reliability and performance, however purely experimental characterization is impractical; predictive models are necessary for optimizing systems and extrapolating short-term experimental results (14).

Since diffusion seems to be a lesser-well-understood property but with potentially disastrous consequences, it is my hope that this guidance will be a useful addition to the design engineer's toolbox that will improve material selection in marine hardware systems.

CHAPTER 2: DIFFUSION FLOWCHART TOOL

INTRODUCTION

The entirety of the flowchart process used to solve polymer-penetrant diffusion problems in marine hardware can be grouped into three parts (Figure 1): 1, forming the problem; 2, identifying the math and choosing a solution method; 3, applying a solution method and solving for what you want.
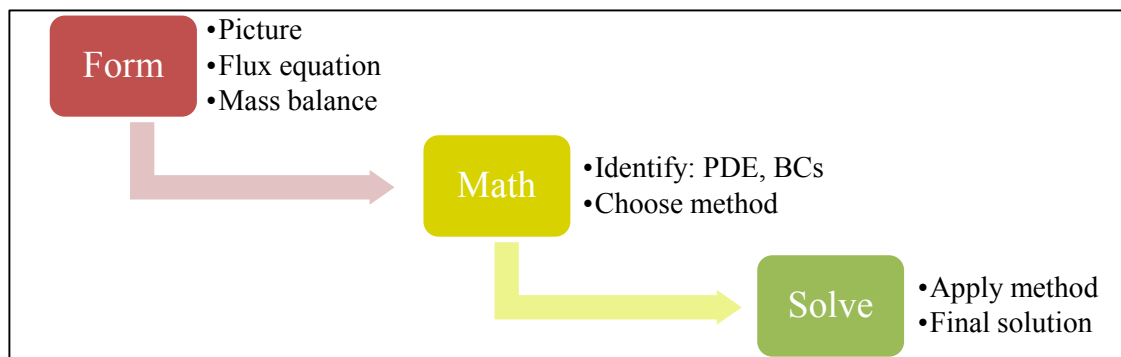
Figure 1 Flowchart process overview

Within each part are a sequence of steps that are to be followed in roughly the given order, with some exceptions noted in the detailed summaries. Table 1 provides an outline to this flowchart process.

This flowchart tool was developed through review of the following relevant textbook literature on the subject of diffusion: Stastna & De Kee (8), Vieth (7), Crank & Park (5) (15), Cussler (1), Neogi (9), Bird-Stewart-Lightfoot (16), & Geankoplis (17).

FORM THE PROBLEM	
Step 1	Clearly define the desired solution (what 'u' want).
2	Draw picture(s).
3	Define initial and boundary conditions.
4	Define the constitutive equation for species flux.
5	Conduct a shell mass balance.
6	Form the differential equation.
IDENTIFY THE MATH & SELECT A SOLUTION METHOD	
Step 7	Identify the type of differential equation.
8	Identify the types of initial & boundary conditions.
9	Select the appropriate solution method.
APPLY THE SOLUTION METHOD & SOLVE FOR WHAT YOU WANT	
Step 10	Apply the solution method.
11	Verify the final solution satisfies the conditions of the problem.
12	Solve for what you want.

Table 1 Flowchart process outline

FORM THE PROBLEM

The first section, "Form the problem" is perhaps the most relevant to the 'flowchart' concept. It is best approached by answering a series of questions, following a 'decision-tree'-like path.

1. Clearly define the desired solution (i.e. what 'u' want).

Start by clearly and absolutely defining the desired solution. In the words of the late, great philosopher Yogi Berra, "You've got to be careful if you don't know where you're going 'cause you might not get there!" (18). This is an important first step as there will be many subsequent steps involving different physical and mathematical concepts, likely prompting one or more reference searches; it is easy to get lost on your way to the solution. Having a clearly defined goal will be like a beacon, always allowing you to return to the original problem at hand. This first step, 'Clearly define the desired solution', is asking the user what 'u' want. To borrow notation from Farlow (19), the notation u, u_x, and u_{xx} are used to describe the dependent transport variable 'u' (e.g. concentration, temperature, velocity) and its first and second derivatives with respect to an independent variable 'x' (e.g. position, time). The user is asked the fundamental question, "What do you want to know?" Typically sought answers in mass transfer are (for a given material species of interest, e.g. 'A') values of concentration ($c_A[x,t]$), flux ($N_A[x,t]$), cumulative amount ($Q_A[x,t]$), and average concentration $\overline{c_A}[(x_0 - x_L), t]$ as a function of position and time. In addition, the time (or position) at which any of the above achieve a certain value of interest may be the desired solution. This latter goal would then be achieved through either algebraic rearrangement of the solution resulting

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from this process; or by some 'solver' method such as Newton-Raphson, Goal Seek (Microsoft Excel), or another root-finding algorithm. These methods are not covered in the scope of this work, but may be necessary in practice especially for any complicated or transcendental functions.

A guide for example questions expected to occur for a marine-hardware-relevant diffusion problem can be found in Appendix 1. It is assumed that users are looking to identify how to solve their polymer-penetrant diffusion-related problem in the sense of fixing it practically, not just how to describe it.

Once the desired solution value is identified, it is critical to answer the question, "How is your desired solution related to the concentration profile?" This is important to establish because no matter what the final desired solution is, the precursor solution necessary to get there (which is developed while following this process) is the concentration profile of the system, i.e. $c_A(x,t)$. For momentum and heat transport problems the analogous precursor solutions are the velocity and temperature profiles, respectively. If the desired solution is the concentration value at a specific position and time, or the time required for the concentration to reach a certain value at a specific position, then no additional relationship is needed. If instead the flux value is desired (usually from a boundary surface), then the key relationship will be the constitutive relationship between species flux and driving force and will inherently incorporate the concentration profile. An important assumption here is that local equilibrium exists between each side of the interface at the boundary. This is true for a system that is 'diffusion limited', i.e. the diffusion through the bulk phase is the slow process. If instead the system is boundary limited then a mass transfer coefficient and interphase

mass transfer solution process is appropriate; this subject is beyond the scope of this work, however more information on it can be found in chapter 8 of Cussler's text on diffusion (1). If the cumulative amount of diffusing species that has moved past a specific position after an elapsed time is desired, then the relationship is the integral of the flux at that position over the cross-sectional area and the elapsed time. For steady-state conditions this will simplify to straightforward multiplication. Finally, the relationship for the average concentration of a region of the system at a particular snapshot in time is the integral over that system dimension at that specific time.

2. Draw picture(s).

An idealized picture of the problem will help to visualize the scenario and link the physical problem with the abstract math used to describe it. A second picture illustrating the macro-system schematic which the simplified problem exists in can be helpful for knowing your problem's place in the larger picture (16), but for the purposes of solving the problem it can be optional. Here the user is asked the question, "What does your physical system look like?"

A guide for example geometries expected to occur for marine-hardware-relevant diffusion problems can be found in Appendix 2.

Drawing the simplified picture will establish the space dimension(s) of the problem. The coordinate system (rectangular, polar, spherical) is chosen based on the simplest shape of the problem relative to what the user wants to know. Polar and spherical coordinate systems are not covered in the scope of this work; however, conversion guidance between coordinate systems can be found in the literature (16). A

useful tip here is to choose the coordinate system direction (i.e. the direction of increasing axis values) to coincide with what the user intuitively believes to be the direction of decreasing concentration, i.e. the net flow direction of the species of interest. For example, the position $z = 0$ should correspond with the boundary location of greatest concentration. This will make the flux positive and the concentration gradient negative in the positive coordinate (z) direction. This approach may not be universally applicable, as shown later on in chapter 4 in one of the worked-through reference solutions from the literature (4).

A good picture will emphasize both the region of interest of the problem and its boundaries. Boundaries and their characteristics are an important part of the final solution; they greatly change its form from one model to the next even if the systems share the same fundamental differential equation. One feature to establish while drawing the picture is to decide if the physical space is an open or closed region, i.e. is one or more direction considered to be of infinite length, or is there finite length to the system? A leaching problem into the infinite expanse of ocean or absorption into a very thick material will likely be semi-infinite and have one space dimension go on to infinity. The behavior of a layer with finite thickness separating two phases will have to be considered as finite length.

These considerations also influence whether a short-time solution or a long-times solution is necessary for the model to be valid. These limits of interest with space and time factor in to the dimensionless ratio $\frac{D_{AB}t}{x^2}$ which influences the convergence of the final solution. If the diffusion coefficient of the system can be determined along with the length and time of interest, then the value of this ratio can assist with choosing

the appropriate solution method later on. Guidance for the validity of one or the other (e.g. short vs. long times) can be found in (20). For a plane surface the short-time solution is valid for $\frac{D_{AB}t}{x^2} < 10^{-2}$. The long-time solution is valid for $\frac{D_{AB}t}{x^2} > 0.5$

3. Define initial and boundary conditions.

Here the user is asked the question, "What is known at the boundaries of the system being modeled?" This is referring to what is or is expected to be known at the boundary positions (space and time) of the system in terms of the following possible values:

Known concentration

The concentration value of the penetrant species of interest is typically specified throughout the bulk of the film at time zero as the initial condition; it may be zero, uniform, or vary as a function of position. The concentration value may also be specified at the boundaries. This is usually specified as constant, but can vary as a function of time at the boundaries. The time-varying case is not covered in the scope of this work, although further guidance can be found in the literature (4) (5). Specifying concentration is simpler in theory, but in practice it can be difficult to determine. The following values are more likely be known:

Known exterior phase value & equilibrium relationship

It is typically easier to know through measurement and to control in practice the bulk concentration of the exterior phase to the system of interest. Translating this to the diffusion system requires an assumption of local equilibrium at the phase boundary and an equilibrium relationship. Local equilibrium implies a steady-state mass balance at

the phase boundary, i.e. flux out equals transfer in, even if there is a discontinuous concentration; that relationship is given by a partition coefficient equation (e.g. Henry's law, $c_A^I = Hc_A^{II}$) and 'hypothetical' concentrations. More information on this can be found in chapter 8, section 5: 'Mass Transfer across Interfaces' of Cussler's text (1). This boundary condition may also be a constant value or can vary with time.

Impermeable

The third boundary condition likely to be encountered is that of the impermeable boundary. This condition implies that no flux of the penetrant species occurs at that boundary position. Mathematically this leads to the relationship that the first derivative of concentration with respect to position is zero at that boundary position,

$$\frac{dc_A}{dx} = 0 \Big|_{x=0 \text{ or } L}$$

A reactive boundary condition may also be specified if a heterogeneous chemical reaction with the penetrant species is occurring. This situation is not explored further in the scope of this work, but example problems can be found in (16), §18.3. In the slow reaction case, final solution of the equation requires the knowledge of the simplifying Taylor series approximation ln(1-x) ≈ -x.

A guide for example initial and boundary conditions expected to occur for marine-hardware-relevant diffusion problems can be found in Appendix 3.

The user, in searching for these known values, will inevitably discover a multitude of different units to describe the concept called 'concentration'. It will be generally helpful (although not critical) to establish these units and a mechanism to enable their conversion so that the final solution can be obtained from this process. In general, values of concentration are described as an amount of material per unit volume

of space, with the 'amount' being in terms of moles or mass of penetrant species. Respective 'fractions' (e.g. mole fraction, mass fraction) may also be encountered, defined as mole/mass of penetrant species divided by the total moles/mass of all material in a given unit volume of space; as a result, the mole/mass fraction term for 'concentration' is dimensionless. Due to experimental convenience, 'partial pressure' values can also be used to describe the 'concentration' of a penetrant species. For practical use of this, an equilibrium relationship is required to convert to other concentration units; the reader is encouraged to refer to the now familiar chapter 8 from Cussler's text (section 5.3) (1).

4. Define the constitutive equation for species flux.

This is the point at which the relationship between the species flux and the concentration gradient is specified, along with any other mechanisms influencing the motion of matter across a fixed plane in space (or appropriate moving reference frame). This relationship is defined in accordance with the user's understanding of what is going on in their system of interest. The curious reader is referred to (16), chapter 24 as a brief introduction to fluxes of mass due to gravity, electric, and magnetic influences; these mechanisms are not covered in the scope of this work. Even if the user is just interested in the concentration profile as their final solution, this is still an important step. The species flux equation will be the bridge between the concentration gradient and the next step, the shell mass balance.

During the development of the diffusion flowchart tool, this step was originally created as 'determine the math' and also included the subsequent step; however it was

later expanded into the more specific steps shown here, prompting users to separately specify the constitutive equation for species flux and the shell mass balance. This was done to give these related but separate concepts the proper space to be more completely grasped rather than lumping them together, as well as making it more convenient to change to a different constitutive equation should the need arise. It is anticipated that complexities involving non-Fickian diffusion (expected with polymer-penetrant scenarios) might be better handled down the road if initially these concepts are treated separately.

A variety of equations to describe this flux and account for these different mechanisms can be found in the literature. At the very least a molecular flux term is expected, and if the bulk medium is a gas or liquid then a convective flux term may be appropriate. Equations including these terms for a mass and mole basis as well as for fixed coordinates and those relative to the velocity of the fluid can be found in (16), table 17.8-2. The marine-hardware-relevant scenarios of polymer-penetrant diffusion occur in solids, so the convective term can be dropped (zero bulk fluid velocity) leaving just the molecular flux term. Barring any other mechanisms of mass transport we arrive at the often-quoted Fick's first law of diffusion,

$$N_A = -D_{AB} \frac{dc_A}{dx}$$

which is analogous to the energy flux equation for conduction of heat in solids.

This step is rather automatic and seems to be without decisions to make. The one question to the user that is important to ask at this time is, "Is the diffusion coefficient concentration-dependent?" If unfamiliar with the polymer-penetrant system of interest, the user will have to look up this sort of interactive behavior in the available

literature. In the likely event that this information cannot be found in sufficient detail (to find a mathematical function for $D_{AB} = f(c_A)$), the user will have to conduct an experiment to determine the relationship between diffusivity and concentration. See the Experimentation section in chapter 3: Diffusion Resources for additional information on this subject.

As routinely stated in the literature the diffusion of penetrants through polymers is markedly concentration-dependent. Many textbook problems in gases or liquids will have as an assumption a diffusion coefficient that is not a function of time, position, concentration, or otherwise; however the tendency is for this to not be the case in solids, especially polymers (1) (5) (16) (21). This feature may be glossed over in the typical instruction of transport phenomena, where mass transfer is often taught in an analogous fashion following heat transfer. This heat analog approach to teaching mass transfer loses the significance of a dependent-variable-varying coefficient, e.g. thermal conductivity changing with temperature, mass diffusion coefficient changing with concentration. In the first chapter of Carslaw & Jaeger's treatise on modeling heat conduction (4), the authors point out that this characteristic is much more pronounced in mass transport than it is in heat conduction, and subsequently deals no further in the text with such nonlinear behavior. Mathematically, the nonlinear differential equation cannot be solved by superposition of elementary solutions as sums or integrals (22). As will be shown through demonstration of the flowchart tool, incorporating the concentration-dependent diffusion coefficient requires advanced solution methods, usually numerical approaches.

This characteristic is important to establish at this point because it will have an immediate impact in the following steps of the process.

5. Conduct a shell mass balance.

Chemists think in molecules, mechanical engineers think in continua; chemical engineers think in both. The equations developed in this process reside in the realm of continuum mechanics; the intricacies of the diffusion coefficient must be traced back to molecular interaction.

This step, based on the concept of conservation of matter, builds the relationship which accounts for the mass of penetrant material in the bulk of the system of interest as a function of position and time. The balance is performed on a 'shell' volume section within the bulk, which is then allowed to shrink to differential thickness; this is then applicable to the entire region between the boundaries. The flux of penetrant 'in to' and 'out of' the shell volume comes from the constitutive equation for species flux defined previously.

Going back to the picture drawn in step 2, a thin slice is added consisting of two parallel plates (or planes) in the middle of the bulk region. The plates are oriented such that the thickness (thin) dimension is in parallel with the anticipated mass diffusion direction; in other words, the plates are perpendicular to the principal direction of diffusion. In their text on transport phenomena; Bird, Stewart, and Lightfoot use the phrase: "thin in the axis direction of anticipated species flux" (16).

What follows then is an accounting for all mass (or moles) of a species within the representative volume. The law of the conservation of matter is used here and it

results in an equation for net accumulation of a species within the volume. This equation has terms for the amount entering the volume, the amount leaving the volume, as well as rates of generation or consumption within the volume in the case of chemical reaction. Each term has units of amount (mass or moles) per time, i.e. a material flow-rate. The amounts entering and leaving the volume are tallied by multiplying each area of the face across which transport is occurring with the flux of that species at that face, then summing the results. The faces in and out are those of the plates at 'z' and 'z+Δz', respectively.

(Mass Flow Rate)$_{in,z}$ - (Mass Flow Rate)$_{out,z+\Delta z}$

+ (Product Production Rate)$_{rxn}$ – (Reactant Consumption Rate)$_{rxn}$

= (Mass Accumulation Rate)$_{vol=A\Delta z}$

In order to complete the shell mass balance, the user must answer the following two questions:

Steady vs. Unsteady State

Based on their system of interest, the user must decide if the concentration of penetrant is changing with time over the region of the system. If not, then the system is at steady-state and there will be zero accumulation within the shell. Otherwise, the system is unsteady (i.e. dynamic) and a time derivative must be incorporated in the shell balance. A consequence is that the mass accumulation rate within the volume is not zero, i.e. $\frac{dc_A}{dt} \neq 0$.

Chemical Reaction

If the penetrant species is reacting in this system, then a reaction rate term (gain or loss) must be included in the mass balance. If the reaction is homogeneous (i.e.

occurring throughout the bulk region of the system) then this term is included in the balance. If the reaction is heterogeneous (i.e. occurring at the system boundary/phase interface), then the reaction rate is not included here and is instead defined in the boundary conditions. Reactive boundary conditions are not covered in the scope of this work.

As the volume thickness is allowed to approach zero, a derivative relationship with respect to position is developed between the fluxes at the opposing faces. This is where the concentration-dependence of the diffusion coefficient will be important, as is described in the next step.

6. Form the differential equation.

Combining the results of the previous two steps will generate the differential equation that is to be solved in the rest of the process. Plug the constitutive equation for species flux into the flux term from the shell balance and take the derivative, resulting in a differential equation with concentration as the dependent variable. This equation will be analyzed in the next part of the process; re-writing it into standard or general form (19) (23) will facilitate the analysis in the later steps.

For a constant diffusion coefficient, the usual instruction is to bring it outside of the derivative and simplify the overall equation. However, if the diffusion coefficient is expected to vary with concentration then this cannot be done, resulting in a nonlinear differential equation. Table 2 illustrates this difference.

Step 4	$N_A = -D_{AB} \dfrac{dc_A}{dx}$	
Step 5	$\dfrac{\partial c_A}{\partial t} = -\dfrac{\partial}{\partial x}(N_A)$	
	D$_{AB}$ constant	**D$_{AB}$ = f(c$_A$)**
Step 6	$\dfrac{\partial c_A}{\partial t} = D_{AB}\dfrac{\partial^2 c_A}{\partial x^2}$	$\dfrac{\partial c_A}{\partial t} = \dfrac{\partial}{\partial x}\left(D_{AB}\dfrac{\partial c_A}{\partial x}\right)$

Table 2 Constant versus concentration-dependent diffusion coefficient

IDENTIFY THE MATH & SELECT A SOLUTION METHOD

The differential equation resulting from the previous section will now be classified. This classification combined with the nature of the boundary conditions and any initial conditions will determine the solution method most appropriate for solving the differential equation. Here, the 'solution' will consist of an expression for species concentration as a function of position and, if applicable, time.

7. Identify the type of differential equation.

Differential equations are classified by the following characteristics (19):

a) Order

b) Number of independent variables

c) Linearity

d) Homogeneity

e) Coefficients

Certain solution methods will only work for differential equations of a certain type. For example, the method of the integrating factor is only applicable to first-order ordinary linear differential equations with continuous coefficient functions (23). The differential equation must have these characteristics or be transformed into one having them before the integrating factor method can be applied.

Arranging the differential equation into general form is helpful for this evaluation. Differential equation characteristics include the order of the differential equation, the number of independent variables (1-ordinary, $\geq$ 2-partial), its linearity and homogeneity, and the dependence of coefficients with respect to the independent

variables.   The additional linearity characteristic found in (24) of quasilinearity describes a PDE with coefficients that are a function of the dependent variable and/or any of its derivatives of lower order than that of the differential equation; nonlinear PDEs therefore have coefficients that are a function of the derivatives of the dependent variable and are the same order as that of the differential equation.

Linear 2nd-order PDEs can be categorized by basic type: parabolic, hyperbolic, and elliptic.   This feature is determined by the resulting value of the following calculation involving the coefficients of the general form of the PDE:

$$B^2 - 4AC = \underline{?}$$

…with A, B, and C coefficients from the linear 2nd-order general equation of dependent variable 'u' (19):

$$Au_{xx} + Bu_{xt} + Cu_{tt} + Du_x + Eu_t + Fu = G$$

The linear unsteady-state diffusion problem (heat and mass) will in general be parabolic, i.e. $B^2-4AC=0$ (19) (24).   If 2 space dimensions are considered, then an elliptic differential equation will likely result.

It is prudent at this point to also identify the ranges of the independent variables over which this PDE applies, i.e. the bounds of the space and time variables.   This is important as it will determine the applicability of some solution methods later on.

8.   Identify the types of initial and boundary conditions.

Prior to this work the author did not fully appreciate how terribly important the initial and boundary conditions are to the final solution of the problem.   The addition of a separate step focused on boundary condition identification seeks to make that clear for future users who have a similar under-appreciation.   The literature suggests three aspects

for classifying the types of boundary conditions in the diffusion problem (19) (24); in the author's opinion the latter reference has a more straightforward breakdown.

First, the overall problem is classified based on the ranges over which the independent variables (e.g. position and time) are allowed to vary. If at least one of the independent variables has an open region (i.e. is allowed to vary to positive or negative infinity), then the overall problem is classified as an initial-value problem. The common example of this is the time variable, which is usually allowed to increase towards positive infinity. This can also be the case for the space variable in the examples of infinite ($-\infty < x < \infty$) and semi-infinite ($-\infty < x \leq 0$] or [$0 \leq x < \infty$) media. If instead the independent variables all vary over a closed region, then the overall problem is a boundary-value problem (24). Farlow (19) suggests distinguishing an infinite media problem as an initial-value problem and all others with at least one open independent variable range as an initial-boundary-value problem. The second worked-through problem discussed in chapter 4 is therefore classified as an initial-boundary-value problem because it is physically bounded but occurs at unsteady-state.

Second, the behavior of the dependent variable (e.g. concentration) at the boundaries is classified. Three different behaviors are considered here, resulting in the following named types of boundary conditions of a problem (24). A boundary condition of the 'first kind' is called a Dirichlet condition, and specifies the value of the dependent variable (e.g. concentration) for a particular value of an independent variable (e.g. position). The dependent variable may be constant, or a function of independent variable(s) (e.g. time, position). This also describes the typical kind of initial condition encountered in simplified diffusion problems (i.e. a specified initial concentration

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profile). Although simpler to model, experimentally determining this value exactly at the boundary region is terribly difficult (1). It is more practical experimentally to specify and control an exterior bulk concentration value instead and use a local equilibrium relationship, e.g. Henry's law, to define the boundary just inside the phase of interest for the problem. The boundary condition of the 'second kind' is called a Neumann condition, and specifies the value of the *derivative* of the dependent variable (e.g. concentration) with respect to an independent variable (e.g. position) for a particular value of an independent variable (e.g. position). This derivative may be constant or a function of independent variable(s) (e.g. time, position) just like the Dirichlet condition. One example is when an impermeable boundary is specified; in this case, the species flux at the boundary is set to zero. Finally, a boundary condition of the 'third kind' is called a Robin condition, and specifies a relationship between the dependent variable (e.g. concentration) *and* its derivative with respect to an independent variable (e.g. position) for a particular value of an independent variable (e.g. position). Examples of this include when flux at the boundary is dictated by a mass-transfer coefficient and the difference between the concentration at the interior surface and the concentration in the exterior bulk, as well as when a concentration-dependent heterogeneous reaction is specified at a boundary surface (16).

Third, linearity and homogeneity are two characteristics used to classify boundary conditions, much as they are used to describe differential equations. The applicability of a solution method may depend on these characteristics of the boundary conditions. See Appendix 4 and relevant math textbooks (19), (23), (24) for some guidance on applicable solution methods.

All of these different types of boundary conditions are expected to be encountered when solving diffusion problems.

9. Select the appropriate solution method.

Having prepared the differential equation from the mass balance and constitutive equation for species flux, and determined the boundary conditions from the picture and problem description, the next general step for the user is to choose a solution method. There are many different methods by which a differential equation may be solved, some better than others for a particular scenario; a helpful guide on the variety was found in (19). The challenge presented here to the practicing engineer is to choose a solution method that will be successful and will give an accurate answer in a reasonable amount of time without being overly complicated. It was assumed by the author that in order to do this, the characteristics of the differential equation and boundary conditions need to be analyzed. At the very least, the initial goal here is to ensure a solution method is chosen that will ultimately be successful and not doomed to fail from the start.

Two options lie before the flowchart user now that they are armed with the knowledge of the differential equation, initial and boundary conditions, and their classification: search the literature for an already worked-out problem with the same equation and condition (or some analog), or determine the appropriate solution process for solving the problem directly. A brief summary of the advantages and disadvantages of each approach are presented in Table 3.

	PRO	**CON**
Look it up	Less work. Likely validated with links to relevant data.	May not exist. Still need to translate notation, mind assumptions.
Solve it yourself	Better understanding. Only limited by mathematical prowess.	May take a long time if not familiar with solving differential equations. Prone to frustration.

Table 3 Solution method decision: look it up versus solve it directly

The example scenarios used to illustrate the flowchart process tool in action will be presented with the latter option chosen, however any reference solution found will also be presented along with the appropriate conversions necessary.

To progress down the path of self-solution, what is desired at this point in the flowchart process is a straightforward continuation of steps to follow leading directly to the appropriate solution. Mathematics being logical, this should be the case at least conceptually, if not theoretically. In practice, however, the diversity of solution methods and their various rules of applicability add a degree of complexity which is outside the current scope of the author's practical mathematical knowledge. The paraphrase "experience will enlighten" seems to be the go-to panacea to address this shortfall; the author finds this frustrating given the aforementioned logical permanence of math and the inability to directly program the fuzzy concept of 'experience' into a computer or translate into a flowchart tool. An attempt to capture this is available in Appendix 4, which seeks to provide a guide for determining the appropriate solution method. Further iterations through the developing flowchart tool will hopefully bring

this enlightenment; as a consolation, the various worked-out solutions should prove useful down the road.

When this flowchart process results in a linear ordinary differential equation, a helpful reference for analytical solution methods is (23). Such is the case for steady-state flux at a point in the bulk phase. First order linear ODEs can be solved by formation of the integrating factor. Second order linear homogeneous ODEs with constant coefficients can be solved by finding the roots of the characteristic equation; inhomogeneous equations of this type require the method of undetermined coefficients or the method of variation of parameters. Others before me have developed their own flowchart diagrams describing the solution methods for general ODEs (25) and specifically for second order linear ODEs with constant coefficients (26).

When this flowchart process results in a linear partial differential equation, a helpful reference for analytical solution methods is (19). Qualifying examples for this situation are unsteady-state (i.e. dynamic) solutions of the concentration profile. The method of separation of variables can be used to solve linear homogeneous partial differential equations with variable coefficients; the Laplace transform can be used to solve linear inhomogeneous partial differential equations, but requires constant coefficients.

When this process results in a nonlinear ordinary or partial differential equation (which may be most of the time), a helpful reference for numerical solution methods is (24). Expect to encounter this when modeling a scenario with a concentration-dependent diffusion coefficient. For a nonlinear ODE of the initial-value problem type, the Euler, modified Euler, and Runge-Kutta numerical methods may be used, although

care should be taken to check their expected accuracy. For a nonlinear ODE of the boundary-value problem type the shooting, finite difference, or collocation numerical methods may be used. For difficult linear parabolic partial differential equations the implicit finite difference, explicit finite difference, or method of lines may be used. Finally, for nonlinear partial differential equations the finite difference discretization results in sets of nonlinear algebraic equations which may be solved using the Newton-Raphson method for simultaneous nonlinear equations.

Farlow (19) describes pros and cons of analytical vs. numerical methods, and makes the point that analytical solutions provide the insight to how physical parameters, initial and boundary conditions affect the solution. If parameter identification from data analysis (such as calculating the diffusion coefficient from experimental data) is the desired goal then the analytical method is the preferred choice; numerical parameter identification is possible but requires optimizing iterated numerical solutions over ranges of parameters to make the best fit to the data. However, it is advised that practically all nonlinear PDEs are impossible to solve analytically and must be solved by numerical methods. Error propagation and stability must be considered when using numerical methods (24). Software such as Microsoft Excel® can assist with performing numerical techniques for simple situations. For advanced problems the software MATLAB® (and its open-source counterpart GNU Octave) may be used. Other software exists which is geared towards solving transport problems and has many numerical techniques built-in, such as COMSOL® (and its open-source counterpart MOOSE Framework).

10. Apply the solution method.

More of a continuation of the previous step than a separate step altogether, it has nevertheless been segregated to emphasize the importance of completely making the choice of solution method before starting down the path of one. This is because the selected method may not ultimately lead to a satisfactory solution, and it is presumed easier to backtrack & try an alternate method if the separate attempts can be more completely isolated. Separate sheets of paper, refreshed whiteboards, et cetera are recommended.

The user may decide to look up a worked-through solution. This will likely involve translating notation and converting units. Cussler's text, §3.5 (1) contains a guide for using references in this manner. Crank's text (5) contains a guide for using references on heat transfer as analogs to mass transfer. Carslaw & Jaeger's text (4) contains a wealth of worked-through solutions for various heat transfer scenarios. Key points to look out for are the signs of the fluxes (indicating direction) and conditions such as equilibrium at the boundaries.

If the user is solving the differential equation themselves or if no worked-through solution is found, then consult the respective references in step 9 for the type of differential equation developed and the type of initial and boundary conditions chosen. Use the dimensionless ratio $\frac{D_{AB}t}{x^2}$ to help determine the limits of validity with resulting solutions and the time and space step size of a numerical method, if applicable.

11. Verify the final solution satisfies the conditions of the problem.

Take the final solution equation of concentration profile and validate the original PDE, BCs, and IC going into section 2 of the flowchart tool (5). This is accomplished by plugging in the final concentration profile solution for concentration (and its derivatives) and checking if both sides of the PDE, BC, and IC equation match. In addition, consider extremes including zero position and time as well as infinite time (and position, if applicable). When a looked up (i.e. similarity) solution is used, pay particular attention to the limits of applicability such as short versus long times. The dimensionless parameter $\frac{D_{AB}t}{x^2}$ can be used to make this distinction.

12. Solve for what you want.

With a validated concentration profile, the user is finally prepared to calculate the value they were originally interested in at the outset of this process. In addition to the concentration value at specific positions and times, the concentration profile can also be used to calculate the average concentration in a bounded region, as well as the flux of the species through a cross-section at a specific position. Refer back to the equation developed in Step 1 relating the value of interest to the concentration profile.

There will be parameters in this final equation (e.g. thickness or other dimensions, the diffusion coefficient) that will need to be specified or obtained by some method. Refer to Chapter 3: Diffusion Resources for a more detailed description of the following sources of this information.

A database or text reference of diffusion coefficients is a natural first resource, however be prepared not to find data for the specific species pair of interest. Even if

there is, the temperature of the data may be different from the application, and the user may be hard pressed to find a detailed model of the diffusion coefficient's temperature dependence for their situation.

Computer simulation of chemical pairs leading to accurate diffusion coefficient prediction of penetrants in polymers is still in development; greater confidence exists in the ability to predict relative diffusion rates of different penetrants in polymers.

Experimentation will likely be necessary to obtain an accurate value for the diffusion coefficient. A wide variety of experimental methods have been developed for the purpose of measuring diffusion coefficients, some of which can be found in §5.6 of (1), organized by utility, accuracy, difficulty of operation, and cost.

A few final checks before calculating the value of interest is to double-check that the units of the obtained parameters will match the units of the final solution equation. If looking for a value requiring a thermodynamic conversion, e.g. going from moles or mass of a species to a pressure or volume value, be sure to clearly state the model used and its limitations. Further advice on this matter is outside the scope of this work.

If looking for the time or position at which a specific concentration value is achieved, an algebraic rearrangement of the equation developed with this flowchart tool may not be possible, especially if transcendental or infinite series functions are involved. In this case, equation 'solver' methods such as Newton-Raphson, Goal seek (Microsoft Excel), or another root-finding algorithm (or graphical solution method) may need to be used.

Congratulations! You have calculated your desired value based on a diffusion-related process!

GENERAL GUIDANCE

Along the way towards developing the flowchart tool and working through problems a few pitfall experiences were gathered. This section seeks to convey the 'lessons learned' from this to a user intent on solving polymer-penetrant diffusion problems.

General approach pitfalls

The first pitfall to avoid is having inappropriately set expectations at the outset regarding the time required, number of different concepts engaged, and number of steps that must be taken to get a functional solution to a polymer-penetrant diffusion problem. A user who is used to one-step solutions involving a quick reference look-up will be frustrated when their problem's complexity is one step greater than the solutions found in the reference; the permutations of solutions possible for different scenarios of boundary conditions and geometry are so large that one shouldn't expect to find the right answer to their specific problem (in a timely fashion) simply by scanning examples in the text.

This process will take some time, multiple pieces of paper, and quite a few whiteboard erasure iterations. Multiple steps and mini conclusions along the way preclude keeping the whole problem 'in one's head,' discouraging the use of shortcut strategies. In addition, seemingly small differences in scenarios (e.g. axis direction, short vs. long times) lead to different solutions almost incomparable in form that appear

dissimilar and unrelated. As such, the user must attack these types of transport problems with a methodical approach; scanning textbooks grasping at straws for a shortcut solution will inevitably lead to frustration and failure.

Differential equation pitfalls

There are a few pitfalls to be aware of when the user is at the stage of solving the differential equation created in the first portion of the process.

When using a solution method (e.g. separation of variables) ensure the method is valid for the scenario. For example, the method of separation of variables requires homogeneous boundary conditions; if the user does not first transform their nonhomogeneous boundary condition then they will have to re-do the work. Chapter 7 of Farlow's text (19) illustrates this and briefly covers the applicability of some solution methods to different scenarios.

Solving differential equations may involve developing equations then plugging those equations into other differential equations. The pitfall to avoid here is forgetting to conduct the differentiation after substitution. This situation is likely to surface when using the method of the Laplace transform as there are a number of intermediate equations and substitutions.

Crank's treatise on the mathematics of diffusion (5) includes a chapter (8) on the (at the time) rapidly expanding field of numerical methods to solve differential equations. Crank recognizes the absence of numerical technique in traditional mathematical instruction; as such the chapter is geared towards non-mathematicians and illustrates some of the pitfalls to avoid when implementing this solution technique.

Non-dimensionalizing variables is more good practice than pitfall avoidance. Crank advocates the technique in particular for use with numerical methods, primarily because sets of different solutions can be obtained by scaling, and "…fundamental parameters are often highlighted and analogies with physically different systems become clearer…" (5). Non-dimensionalizing reduces the problem to pure math, so solution attack is not clouded by parameters specific to the field of study (19). In addition, non-dimensionalizing variables can assist with analytical solution methods by enabling math 'tricks' to be used. For example, non-dimensionalizing physical boundaries so that a space region varies from 0 to 1 as opposed to 0 to L enables the use of orthogonality to simplify some series summations of orthogonal functions.

The guidance encourages developing the boundary conditions early, even if initially they are done descriptively without numbers or equations. This emphasis seeks to bridge the gap between the physical situation (grasped by most spatially-minded humans) and the abstract math which will be solved to describe it (not intuitively grasped by most humans, including some nascent chemical engineers). Also, a loose rule of thumb when applying boundary conditions using analytical solution methods is to apply the homogeneous boundary condition first.

Unit pitfalls

Double-check units along the way. If the units are not working out to that which is expected, then there is likely an error. It is good practice to check units at each mini-conclusion in the process (e.g. constitutive equation for species flux, shell mass balance, boundary conditions). At the very least, this must be done at the end when getting back to solving for the value of interest for the problem (27).

With many different ways to describe just the value of concentration, unit conversion will almost certainly need to be implemented prior to the successful conclusion of the problem. A comprehensive table of unit conversions can be found in the text by Bird, Stewart, and Lightfoot (16), as well as in texts by other authors on the subject.

CHAPTER 3: DIFFUSION RESOURCES

INTRODUCTION

The parameters required by the equations resulting from the aforementioned flowchart tool must be obtained from somewhere. The goal of this section is to describe where the user can find this information. Database or databank resources are a natural first choice, as the dirty work has already been done. However the user may not find their particular polymer and penetrant material pair under their particular set of environmental conditions; to find matching polymer molecular weights, degree of crystallization, thermal history, and other permutations is even more unlikely. A closest match may have to be used with assumed deviation, or the user can try a predictive approach through simulation. On a limited basis molecular dynamics simulation and other methods can be used to roughly predict transport properties and other polymer parameters should the user need to screen a large number of different options. With this narrower field of candidates, or perhaps in the case of a constrained system, the user will inevitably have to turn to experimental methods to get the final answer. A host of experimental techniques exist which can measure the phenomenon of mass diffusion, many of which are inappropriate for the types of polymer-penetrant systems of primary interest here. The two dominant methods of gravimetric sorption and time lag/permeation technique will be described herein, with some reference to other possible methods. Of particular interest is the experimental technique which elucidates the relationship between diffusion coefficient and concentration for a concentration-dependent-diffusion-coefficient; obtaining this expression is key to incorporating this significant characteristic of diffusion in polymers into a predictive model for a system.

Finally, some general resources related to diffusion are briefly reviewed, focused on reference material for solving differential equations as well as where to turn to for worked-through solutions of the diffusion problem for various scenarios, geometries, and boundary conditions.

DATABASE RESOURCES

Print resources

Textbooks on the subject of diffusion in polymers have some experimental records throughout them (7) (8) (15), however they are not in general designed to be databanks of experimental results. Larger volumes/compilations designed to tabulate such data exist and tend to be a few editions in at this point (28) (29) (30). The section on permeation in the Polymer Handbook tabulates mostly permeability, but intermittently includes information on solubility, and diffusivity. The McKeen text tabulates permeability and the less-generic vapor transmission rate, with no data on solubility or diffusivity. Both references contain little to no data on polyurethane materials, an important family of polymers to some marine hardware systems.

The references just mentioned as well as those throughout the literature all use a variety of different relatable parameters to report transport phenomena results. Examples include the transmission rate, the permeation rate, the permeance, the diffusion coefficient, the solubility, and the permeability coefficient. These parameters may be derived from the others using values associated with the experiment that was run (e.g. thickness, temperature and the penetrant partial pressure) and by making assumptions (e.g. permeability coefficient is independent with thickness). Figure 2 is a

guide to deriving permeation parameters from those available based on their interrelationships (31).
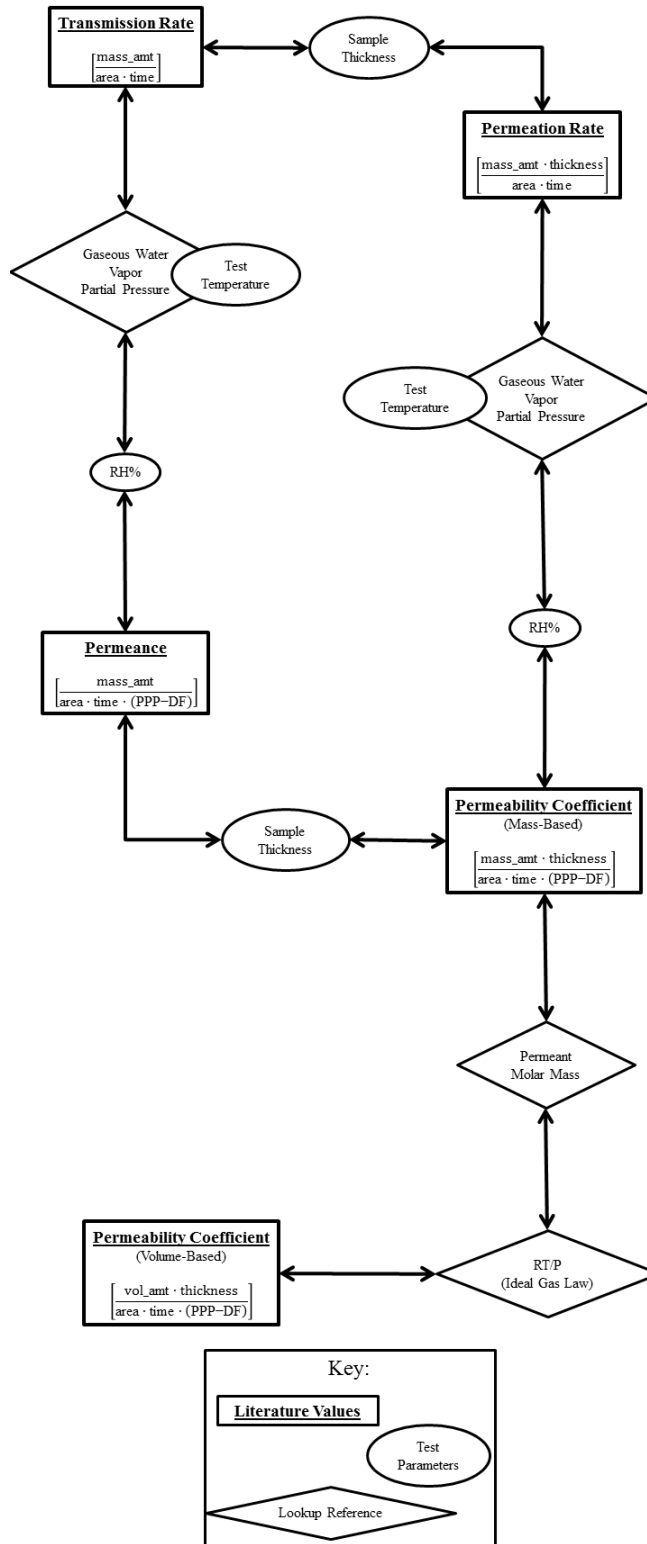
Figure 2 Roadmap of permeation parameter conversions (31)

Each parameter may also be reported using a variety of different units, some of which by convention include members of both the English system and the Metric system of units (e.g. permeation rate: gram·mil·m^{-2}·day^{-1}). The permeability coefficient units can be particularly confusing:

$$P \; [=] \; \frac{cm^3 \cdot cm}{cm^2 \cdot s \cdot Pa}$$

with a volume, a length, and an area unit all within one parameter and no unit cancellation, and a pressure (but not ambient pressure – it's the penetrant partial pressure driving force across the membrane). Expect to perform unit conversions and to not be able to use literature values directly as they are found.

Digital resources

Due to the sheer number of permutations of polymer-penetrant scenarios, print records are ultimately physically incapable of conveniently containing the majority of tabulated properties of possible polymer-penetrant pairs. Computerized resources with remote, online access are a practical alternative to printed tables, not to mention the search and analytical advantages of digital records. The free website MatWeb (32) can be a helpful start. Other free resources include subsets of MatNavi (33), the NIMS materials database from the Japanese National Institute for Material Science. Commercial database products available include the Dortmund Data Bank (34), AIChE's Design Institute for Physical Properties (35), Granta Design's GRANTA MI^{TM} and library, and the simulation-based database Mol-Instincts (36). The user is strongly encouraged to investigate whether the particular database product is appropriate for their application.

There is an ongoing White House level directive called the Materials Genome Initiative (www.mgi.gov) which has as one of its tenets the goal of facilitating access to computerized materials data (see https://www.mgi.gov/strategic-goals/facilitate-access-materials-data). A number of digital database systems are involved in this effort which compile empirical and simulation-based material property information. Examples include The Materials Project, the Materials Data Curation System (MDCS), Automatic Flow for materials discovery (AFLOW), and the Center for Hierarchical Materials Design (CHiMaD).

SIMULATION

Molecular dynamics simulation is a potential avenue towards predicting diffusion behavior. It has been suggested historically as a promising option (8). Keffer's research has proposed a route to diffusion coefficients through these simulations (37). Molecular dynamics simulation or theoretical predictive models of diffusion (38) (39) could also provide a relationship for a diffusion coefficient dependent on concentration, incorporating polymer-penetrant interactions (40).   In general, using computer simulation to predict polymer-penetrant diffusion coefficients that are sufficiently accurate for application is still an active challenge; more confidence can usually be made in predicting relative differences of penetrant behavior within a polymer type (41).

EXPERIMENTATION

Multiple authors (1) (5) (42) (43) have reviewed possible experimental methods for measuring diffusion; some have focused on methods more appropriate to polymers (15). The two types of methods primarily used are those based on permeation and those

based on gravimetric sorption and/or desorption. Permeation experiments can provide the permeability and the diffusion coefficient (for ideal behavior) (31), while sorption/desorption experiments result in the diffusion coefficient and solubility (44). The permeability is the product of the diffusion coefficient and the solubility.

Examples of permeation equipment are instruments produced by MOCON and Systech, (45) (46) designed to measure gases and vapors (such as oxygen, carbon dioxide, and water) through thin polymer films. The gravimetric sorption/desorption method can be simply conducted via immersion if the penetrant is a liquid, or by dynamic vapor sorption for deposition of the penetrant from the gas phase; one example of instrumentation for the latter method is produced by Surface Measurement Systems (47).

An important simplifying assumption in the theoretical background of the parameters derived from the experimental methods just mentioned is that of constant diffusion coefficient. Corrections must be made or alternate methods employed should the diffusivity vary with concentration. One method of interferometry (requiring transparent samples) is promoted by Cussler (1) as being the 'best' for measuring concentration-dependent diffusion. Crank (5) references a technique described by Duda and Vrentras (48) which enables the determination of the concentration–dependence of the diffusion coefficient from a single sorption curve measurement. Crank and Park (15) allude to determining this dependence from sorption rate, and time lag measurements. From sorption measurements, a series of experiments run at successively smaller intervals of uniform initial concentration can be used to determine the relationship between the diffusion coefficient and the concentration (49). At the

very least, the equations for a constant diffusion coefficient can be used and the resulting value will be an average of the diffusion coefficient values for the range of concentration tested. The dependence of the diffusion coefficient on concentration can be determined from time lag measurements, however the fundamental relationship between D and C must be known *a priori* (50). Just as a warning, it has been reported that the dependence of D on C will be different depending on the measurement technique chosen (51).

GENERAL DIFFUSION REFERENCE

Textbooks guiding users in the solution of partial and ordinary differential equations exist focused on analytical methods (19) and numerical methods (24). The treatises on mass diffusion (5) and on heat conduction in solids (4) both contain many worked-through simplified problems (although they are by no means simple) for various geometries, scenarios, and boundary conditions in transport phenomena.

CHAPTER 4: DIFFUSION PROBLEMS

INTRODUCTION

Examples of diffusion problems that are likely to be useful to the user are those of the membrane geometry with specified or impermeable boundary conditions. These scenarios can be used to describe diffusion through simplified 'container' structures (cylindrical hoses, layered boxes, etc…) and coatings, respectively. Descriptions of the process to solve these diffusion problems using the flowchart tool are presented in their entirety in order to convey to the user the true scope of the effort involved. Their influence on the development of the flowchart tool is described to explain its origins. The complexity introduced when considering a concentration-dependent diffusion coefficient is demonstrated in part using the flowchart tool, with guidance to the user for additional references. The fundamental theory thus far has considered the bulk material to be homogeneous, however the practical applications of the user will inevitably require heterogeneous composite materials to be considered. The promising technology of nanoclay platelet filler material will be touched upon here from the standpoint of solving the diffusion problem; a more complete description of the topic will be delved into in the subsequent chapter. Finally, two additional marine-hardware-relevant scenarios of likely interest will be briefly described but not solved.

STEADY-STATE, PLANE SHEET, SPECIFIED BOUNDARY CONCENTRATION

Introduction

The first problem to work through was that of steady-state diffusion through a plane sheet. This scenario is found in the experimental determination of the diffusion

coefficient through the time-lag method, and it is straightforward to work through with examples found directly in the literature (5). This problem was worked through in two ways: by general but not identical textbook guidance (16), and then by comparison to the identical problem solution in the literature (5). The concept of nondimensionalizing the problem was also introduced (52).

In this first effort the generic constitutive equation for species flux was obtained from the literature (16) and simplified through assumptions (e.g. no bulk flow, so no bulk velocity, so no convective flux term). Since this will be true for the scope of diffusion of penetrants in solid polymers, the guidance developed in this thesis was amended to only consider the molecular diffusive flux term when defining the equation for flux of penetrant (step 4 of the flowchart tool).

Application of the flowchart tool

FORM THE PROBLEM:

1. Clearly define the desired solution.
   • How much (mass) of species A will pass through the membrane after time *t*?
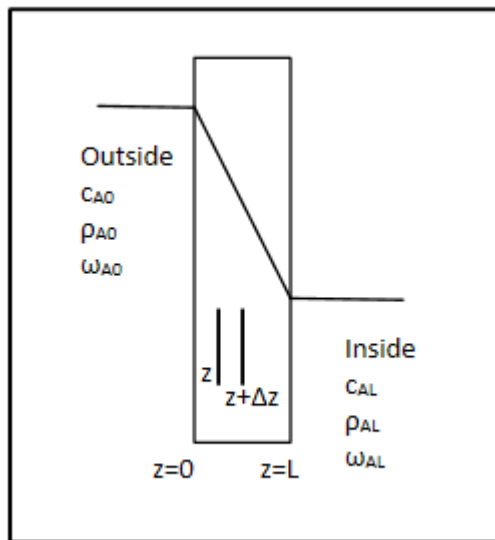2. Draw picture(s). (Figure 3)

Figure 3 Steady-state diffusion problem illustration

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- Roughly define boundary conditions:
  - B.C.1: at z = 0, concentration of species A in the membrane is fixed in equilibrium with the exterior phase.
  - B.C.2: at z = L, concentration of species A in the membrane is fixed in equilibrium with the exterior phase.
3. Define relationship between what you want and the flux.
  - $Q \equiv$ amount (mass) of species A
  - S is the area of the membrane of interest, at position L.
  - Equation relating to flux:
    - $Q = S \int_0^t j_A|_L dt = S j_A t$
    - ...$S j_a t = Q$ for constant (steady-state) flux.
    - $j_A|_L$ is the molecular flux of species A at position L.
    - t is the time elapsed over which you want to know the total amount of A which has passed through the membrane.
4. Define the constitutive equation for species flux.
  - From (16) Table 17.8-2 eqn. (C)
    - $n_A = \rho_A \mathbf{v} - \rho D_{AB} \nabla \omega_A$
    - $n_A|_L$ is the combined flux of species A at position L [=] mass/(area*time).
    - ρ is the density of the medium [=] mass/volume
    - ρ_A is the mass of species A per unit volume in the medium, i.e. the mass concentration of A [=] $mass_A$/volume
    - $\mathbf{v}$ is the mass average velocity of the system [=] length/time
    - D_{AB} is the binary diffusion coefficient (diffusivity) [=] area/time
    - ∇ is the grad operator
      - $\nabla = \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right)$
    - ω_A is the mass fraction of species A [=] ($mass_A$ / total mass of unit volume) [=] dimensionless
  - In this case, convective flux is not anticipated for a solid membrane, so only the molecular flux term is needed.
    - $j_A = -\rho D_{AB} \nabla \omega_A$
    - ...prompting us to update our original equation relating flux to what we want to know.
    - Also, for our 1-dimensional system of interest:
      - $j_A = -\rho D_{AB} \frac{d\omega_A}{dz}$
5. Conduct the shell mass balance.
  - For the thin shell volume indicated in the picture:
  - (Rate of mass of species A...)(In - Out + Generation - Consumption) = Rate of mass of species A Accumulation [=] $mass_A$/time
  - $S j_A|_z - S j_A|_{z+\Delta z} + 0 - 0 = 0$
  - No generation or consumption terms because no reaction.
  - No accumulation term because the region inside the membrane is at steady-state.
  - So:
  - $S j_A|_z - S j_A|_{z+\Delta z} = 0$
  - Dividing by $S\Delta z$ & taking the limit as Δz goes to zero:

- $-\dfrac{dj_a}{dz} = 0$

6. Insert the constitutive equation for flux into the shell mass balance result.
   - Constitutive flux equation:
     - $j_A = -\rho D_{AB}\dfrac{d\omega_A}{dz}$
   - Shell mass balance result:
     - $-\dfrac{dj_a}{dz} = 0$
   - Combined:
     - $-\dfrac{d}{dz}\left(-\rho D_{AB}\dfrac{d\omega_A}{dz}\right) = 0$
     - Simplifying for constant density and diffusivity within the membrane:
     - $\dfrac{d}{dz}\left(\dfrac{d\omega_A}{dz}\right) = 0$
   - Re-written for differential equation analysis:
     - $\dfrac{d^2\omega_A}{dz^2} = 0$

7. Re-define boundary conditions based on units in the differential equation.
   - B.C.1: at z=0, $\omega_A = \omega_{A0}$
   - B.C.2: at z=L, $\omega_A = \omega_{AL}$

IDENTIFY THE MATH AND SELECT A SOLUTION METHOD:

8. Identify the type of differential equation which resulted from the earlier combination of the constitutive equation for species flux and the shell mass balance result.
   - $\dfrac{d^2\omega_A}{dz^2} = 0$
     - Partiality: Ordinary
     - Order: 2nd
     - Number of independent variables: 1
     - Linearity: linear
     - Homogeneity: homogeneous
     - Coefficients: constant (zero)
     - Basic type:
       - General form: (Farlow1993PDE notation)
         - $Au_{zz} = 0$
         - $B^2 - 4AC = (0)^2 - 4(1)(0) = 0$
       - => Parabolic
9. Identify the types of boundary and initial conditions.
   - B.C.1: at z=0, $\omega_A = \omega_{A0}$
     - Dependent variable (ω_A) specified at the boundary.
     - => Type 1; First kind; Dirichlet.
   - B.C.2: at z=L, $\omega_A = \omega_{AL}$
     - Dependent variable (ω_A) specified at the boundary.
     - => Type 1; First kind; Dirichlet.
10. Solution method selection:

- Check literature for worked-out solution with same differential equation and boundary conditions.
  - (5) §4.2, mole basis
    - For this problem, concentration profile is eqn. 4.3 & flux is 4.4.
    - If boundaries are different, such as Farlow's Type 2 (mass transfer coefficient specified at boundary), then the following equations apply for concentration profile and flux, respectively:
      - One boundary Type 1, one boundary Type 2: eqn. 4.3a & 4.4a
      - Both boundaries Type 2: eqn. 4.3b & 4.4b
  - (4) §3.2
    - This reference contains the heat analog to this problem with the flux of heat (analogous to concentration) given as equation (1).
  - (1) §3.5
    - References Crank's solution for the unsteady-state startup condition and where both boundaries are Type 2.
  - (16) §18.2
    - This reference includes the convective flux term as the bounded region is a gas phase.
- Should you fail to find the problem or do not have access to these resources, solve the differential equation with the deduced boundary and initial conditions.
  - This is a second-order ordinary linear homogeneous parabolic differential equation, which means that its solution should be attainable through applying the regular rules of integration twice on the system.
  - The boundary conditions are both Type 1, Dirichlet, so straightforward substitution and algebraic manipulation should allow for the deduction of the two resulting constants of integration.
- The Crank, 1975 reference should be used in this case.

APPLY THE SOLUTION METHOD AND SOLVE FOR WHAT YOU WANT:

11. Apply the solution method.
- To use Crank's method, we must convert notation from the mole basis to a mass basis. Table 4 describes the conversions necessary for the differential equation, and Table 5 describes the conversions necessary for the constitutive equation for species flux.
- Concentration profile:
  - Crank's equation:
    - $$\frac{c - c_1}{c_2 - c_1} = \frac{x}{l}$$

Crank's Notation	Our problem

C = mole concentration of species A
    [=] moles$_A$/volume
	$\rho_A = \rho\omega_A$ = mass concentration of species A
	    [=] mass$_A$/volume

C$_1$ = mole concentration of species A at surface x = 0
    [=] moles$_A$/volume
	$\rho_{A0} = \rho\omega_{A0}$ = mass concentration of species A (just inside membrane) at surface z = 0
	    [=] mass$_A$/volume

C$_2$ = mole concentration of species A at surface x = l
    [=] moles$_A$/volume
	$\rho_{AL} = \rho\omega_{AL}$ = mass concentration of species A (just inside membrane) at surface z = L
	    [=] mass$_A$/volume

x = length coordinate dimension
    [=] length
	z = length coordinate dimension
	    [=] length

l = thickness of region bounded by parallel planes
  [=] length
	L = thickness of region bounded by parallel planes
	  [=] length

Table 4 Steady-state diffusion problem notation conversion, concentration profile

- o Converting:
  - $\dfrac{\omega_A - \omega_{A0}}{\omega_{AL} - \omega_{A0}} = \dfrac{z}{L}$
  - Note: ρ cancels out
- Flux:
  - o Crank's equation:
    - $F = \dfrac{D(C_1 - C_2)}{l}$

Crank's Notation	Our problem
D = diffusion coefficient (diffusivity) [=] area/time	D$_{AB}$ = diffusion coefficient (diffusivity)

F = molar flux of species A
    [=] moles$_A$ / (area*time)
	j$_A$ = mass flux of species A
	    [=] mass$_A$ / (area*time)

Table 5 Steady-state diffusion problem notation conversion, flux equation

- o Converting:
  - $j_A = \dfrac{D_{AB}(\omega_{A0} - \omega_{AL})}{L}$

12. Verify the solved differential equation satisfies the original boundary and initial conditions, and common sense.
    - Concentration profile equation:
      - o B.C.1: at z=0, $\omega_A = \omega_{A0}$

- ○ B.C.2: at z=L, $\omega_A = \omega_{AL}$
- • Flux equation:
  - ○ Common sense
    - • System is at steady-state, so flux is not time-dependent, nor is it spatially dependent (no z variable). Therefore the flux of species A into the membrane should equal the flux of species A out of the membrane.
13. Solve for what you want
  - • Return to the original equation developed relating the value of interest and the flux of species A
    - ○ $Q = Sj_A t$
  - • Substitute:
    - ○ $Q = S\dfrac{D_{AB}(\omega_{A0} - \omega_{AL})}{L} t$
  - • Get parameters you need:
    - ○ S = area of membrane
    - ○ D_{AB} = diffusivity of species A through membrane material B
    - ○ L = thickness of membrane
    - ○ ω_{A0} = maintained mass fraction of species A at z = 0
      - • i.e. the equilibrium value achieved for a constant exterior environment. You may need a Henry's law type equation.
    - ○ ω_{AL} = maintained mass fraction of species A at z = L
      - • i.e. the equilibrium value achieved for a constant exterior environment. You may need a Henry's law type equation.
  - • Solve
14. Congratulations!

Influence on the flowchart tool

Working through the problem with analogous but not identical guidance established the initial flowchart steps to solution stated previously. It also established the connection between identifying the parts of the problem (e.g. differential equation, composed of mass balance and constitutive equation; boundary conditions) and their role in forming the final solution (e.g. differential equation is solved for the dependent variable; boundary conditions are used to determine the constants of integration). Comparing the problem to an identical problem solution in the literature introduced the concept of converting notation (e.g. the initial problem dependent variable was mass

fraction; the literature problem dependent variable was molar concentration) and emphasized the importance of double-checking units in equations (27).

UNSTEADY PLANE SHEET, IMPERMEABLE BOUNDARY

Introduction

The second problem that was worked through was that of unsteady diffusion through a plane sheet, with an impermeable boundary condition specified at one surface and a constant concentration specified at the other. This scenario is found in applications involving coatings over materials impervious to the penetrant (e.g. metals, glass, etc.). Even though the underlying material is impervious to the penetrant, there may be some interaction which is dependent on the penetrant concentration in the material presented to the exterior surface (e.g., corrosion, adhesion).

This was a more complicated problem than the first and prompted significant review of math concepts (differential equations), requiring a working through of other example problems in other textbooks.

Influence on the flowchart tool

Working through this problem revealed unexpectedly (to the author) that two valid solutions applicable over different ranges of the independent variables were possible, prompting an addition to the flowchart tool to account for and guide similar encounters in the future. This arises from different solution convergence rates depending on the value of the dimensionless ratio $\frac{D_{AB}t}{x^2}$.

Description of the worked-through problem

The math notes for the first phase of the flowchart process can be found in Appendix 5. The numbering of the steps do not match because a prior numbering scheme was retained to show how the flowchart process was developed. Time spent forming the problem further refined the flowchart process, establishing the specific step of clearly defining the initial and boundary conditions of the problem. This first section was completed methodically, with no additional surprises encountered.

Step 1: Clearly define the desired solution

The desired value for this scenario is the concentration of species A at the impermeable boundary face after an elapsed amount of time, i.e. the unsteady-state concentration profile. It is imagined there is some threshold value of concentration at this surface which is crucial for a particular application.

Step 2: Draw a picture (Figure 4)
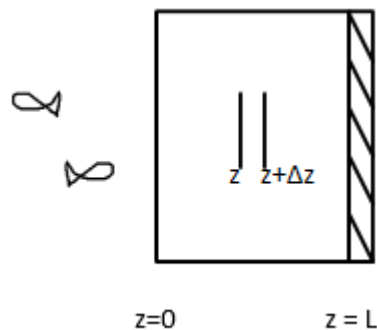
Figure 4 Unsteady-state, impermeable boundary diffusion problem picture

Initially the length axis was set to be increasing in the direction of anticipated net flux of species A. However, this was eventually flipped for one of the final chosen solution methods.

Step 3: Define the initial and boundary conditions

I.C.: at t = 0, all z, $c_A = 0$

B.C.1: for t > 0, z = 0, $c_A = c_{A0}$

B.C.2: for t > 0, z = L, $J^*_{Az} = 0$

Initially, the coating everywhere has zero concentration of species A. After immersion, the concentration of A just inside the surface immediately reaches equilibrium with the exterior environment and remains at that value the entire time it is immersed. No species A leaves the coating at the coating-metal surface, i.e. the flux of A in the positive z direction is zero at z = 0. Qualitatively, if considering the large time solution then at large times the concentration throughout the coating will be uniform and equal to the concentration of A in equilibrium with the exterior environment.

Step 4: Define the constitutive equation for species flux

$$J^*_{Az} = -cD_{AB}\frac{dx_A}{dz}$$

Molecular diffusive molar flux is the only flux anticipated for this scenario. Convective flux is not anticipated because the bulk polymeric coating material is stationary. The diffusion is assumed to be constant and not concentration-dependent, for simplicity.

Step 5: Conduct a shell mass balance

$$-\frac{\partial J_{Az}^*}{\partial z} = \frac{\partial c_A}{\partial t}$$

There is no chemical reaction specified, so no generation or consumption term for species A is required. An accumulation term is expected since this is an unsteady-state problem: over the time range of interest the concentration goes from being zero everywhere to a uniform value, i.e. accumulation occurs.

Step 6: Form the differential equation

$$D_{AB}\frac{\partial^2 c_A}{\partial z^2} = \frac{\partial c_A}{\partial t}$$

The equations from the previous two steps are combined. The diffusion coefficient moves outside the derivative because (in this case) it is assumed constant.

Step 7: Identify the type of differential equation

Identification of the characteristics of the formed problem PDE and BCs was guided by (19), with additional reference to (24). The differential equation for this problem is a second order homogeneous linear partial differential equation with constant coefficients. The linear unsteady-state diffusion problem (heat and mass) will in general be parabolic, i.e. $B^2-4AC=0$ (19) (24), and this is indeed the case for the second worked-through problem.

Step 8: Identify the types of initial and boundary conditions

For the second worked-through problem a homogeneous linear Neumann condition (flux specified) is present at the impermeable face of the plane sheet, and a nonhomogeneous linear Dirichlet condition (concentration specified) is present at the other face.

The initial concentration everywhere is zero (homogeneous linear Dirichlet condition). After solving it is possible to confirm that at long times the concentration everywhere will be equal to the concentration of species A in equilibrium with the exterior environment (if the resulting solution is valid at long times).

Step 9: Select the appropriate solution method

Having identified the type of PDE and BCs, the next step is to choose an appropriate solution method. The first recommended approach is to review the literature for an identical or analogous problem already worked-through. In the case of this impermeable boundary problem, a number of similar examples were found but none looked directly applicable. The initial search of Crank's text (5) revealed a sub-section on impermeable surfaces in the section on non-steady-state diffusion in the chapter on diffusion in a plane sheet geometry (§4.3.8, p.62). However, a solution was not directly given for the boundary conditions of one impermeable face and one face of fixed concentration and was instead referenced as a half-symmetry modification of an earlier equation,

$$C = C_1 + (C_2 - C_1)\frac{x}{L} + \frac{2}{\pi}\sum_1^\infty \left[\frac{C_2 \cos n\pi - C_1}{n} \sin\frac{n\pi x}{L} e^{-Dn^2\pi^2 t/L^2} \right]$$
$$+ \frac{2}{L}\sum_1^\infty \left[\sin\frac{n\pi x}{L} e^{-Dn^2\pi^2 t/L^2} \int_0^L f(x') \sin\frac{n\pi x'}{L} dx' \right]$$

for $C = C_1$, $x = 0$, $t \geq 0$; $C = C_2$, $x = L$, $t \geq 0$; and $C = f(x)$, $0 < x < L$, $t = 0$. Clear guidance for making the modification was not readily apparent, and there also appeared to be a typo in the equation from the book (second summation, first sin() term, was 'π' instead of 'L' in the denominator).

The closest match from the initial literature search was a heat transfer solution in (4),

$$v = V + \frac{2}{L} \sum_{n=0}^{\infty} \left[e^{-\kappa(2n+1)^2\pi^2 L/4L^2} \cos\frac{(2n+1)\pi x}{2L} \left\{ \frac{2L(-1)^{n+1}V}{(2n+1)\pi} \right. \right.$$
$$\left. \left. + \int_0^L f(x') \cos\frac{(2n+1)\pi x'}{2L} dx' \right\} \right]$$

for the case in which the end x = 0 is insulated and the end x = L is kept at V and the initial temperature is f(x). Note that the direction of flux is reverse to the length axis here as compared to the boundary conditions established for this problem. Note also that here the summation starting point is at n = 0, whereas the summations in Crank's equation start at n = 1; perhaps this would be changed when modifying Crank's equation for half-symmetry.

Unfamiliarity with the method of converting a heat transfer solution to a mass transfer solution precluded the immediate adoption of the result found in (4). Guidance for this conversion process can be found in a number of references, e.g. (4) (5) (16), however the experience of developing the solution without using a preconceived one was deemed valuable. Therefore, the approach was changed to applying a solution method appropriate for the formed initial-boundary-value problem.

Step 10: Apply the solution method

A similar problem found in (19) was solved using the method of separation of variables. This was worked through for the text example, and then the same strategy was applied to the impermeable boundary problem; see Appendix 6 for the math notes. In this case, applying the method of separation of variables directly to the formed problem was inappropriate as it cannot be used for a problem where one or more of the

boundary conditions are nonhomogeneous (in this case, the Dirichlet condition of a nonzero concentration specified at the plane sheet surface). This obstacle is surmountable by first transforming the nonhomogeneous boundary condition into a homogeneous one, then solving via separation of variables; this method was attempted for this problem. Although a solution was reached, it was uncertain whether it satisfied the criteria of the problem (PDE, BCs, IC). Additionally, unfamiliarity with the transformed boundary condition approach caused difficulty when applying the inverse transform to return to the original variables of the problem; it was later determined that a mathematical error by the author caused much of the difficulty. More rigorous trial of the solution was postponed in favor of attempting a different, potentially more powerful solution to the formed problem: the Laplace transform.

The theory of the Laplace transform has been covered in a number of textbooks (4) (5) (19) (23) (53). In a nutshell, the goal is to transform a hard problem in original variables into an easy problem in transformed variables, solve it, then apply an inverse transform (via reference tables) to the solution in order to return to the original variables (19). The example problem in the text (19) demonstrating the use of the Laplace transform was worked through, however it turned out to be very difficult at the inverse-transform step to return to the original variables of interest; consulting an alternate reference (53) was required in order to finish the problem. The lesson learned here was that not all textbook example problems are good ones. Continuing on, the Laplace transform method was applied to the impermeable boundary problem. However, the inverse-Laplace transform again proved to be a stumbling block, with an even more complex result to invert than the textbook example problem; no transform pair could be

found in the literature. One lesson here is that the Laplace transform method is powerful, but loses much of its effectiveness when no table of transform pairs contains the particular transformed solution of interest. A later reference was found (22) with particular advice on dealing with the types of transformed equations resulting from using the Laplace transform on diffusion problems; running this obstacle to ground was postponed when further literature searching resulted in discovering an analogous worked-through problem.

A nearly identical worked-through impermeable boundary problem was found in (5) after re-review; it was missed during the initial literature search. Notes from working through this problem in the context of the diffusion flowchart tool are in Appendix 7. The major difference between this problem and the formed problem was the direction of the x-axis (position); in the text, the impermeable boundary was located at x = 0, whereas in the formed problem the impermeable boundary was located at x = L (the thickness of the plane sheet). This key difference made the Laplace transform method easier to solve; it is not understood by the author how this can be predicted at the outset of choosing a solution method. This was not the end of the story, however, as there exist two viable solutions to the original problem depending on whether an expansion in negative exponentials or if a unique partial fraction decomposition is applied to the transformed equation prior to inverting. Each solution is applicable over a different range of time: the solution from expansion in negative exponentials is applicable over short times (verified by the author), and the solution from partial fraction decomposition is applicable over long times, (not verified by the author). Most of the short-times solution was derived by the author with the exception of the component

involving the series expansion by binomial theorem which was glossed over in the text. This concept of working through a problem and ending up with two viable solutions applicable over different ranges of the independent variables was unexpected, and prompted an addition to the process flowchart tool to account for similar encounters in the future.

Step 11: Verify the final solution satisfies the conditions of the problem

The resulting numerical evaluation of the short-time solution is displayed in the overlay Figure 5. The initial condition of zero concentration everywhere is satisfied. The final condition of uniform concentration is not considered here since this solution is only valid at short times. The constant concentration Dirichlet condition at the penetrant inlet face is satisfied. The zero slope of the concentration profile as well as rise in concentration at the impermeable surface testifies to the homogeneous Neumann condition at that face.
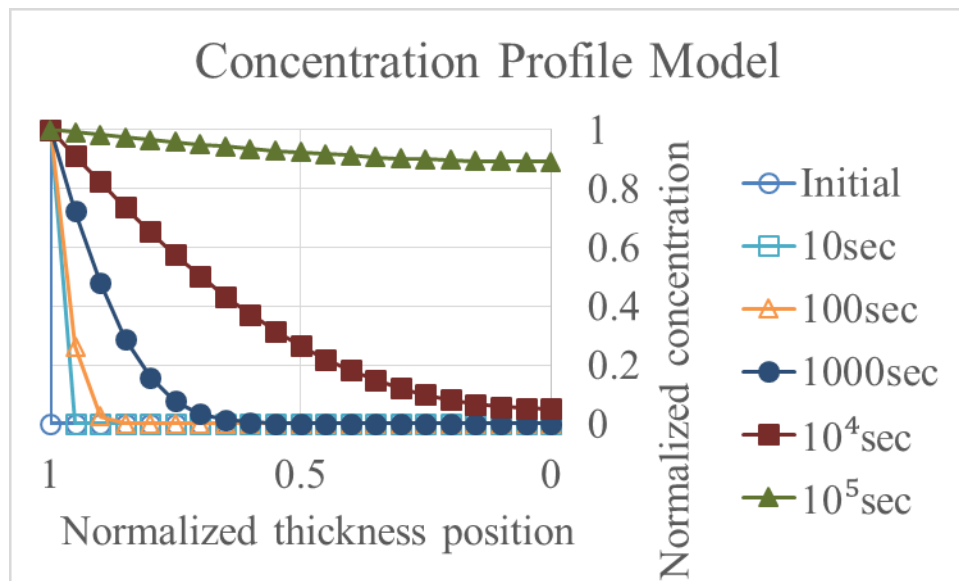
Figure 5 Numerical evaluation of the short-time solution to the unsteady-state impermeable boundary problem.

Step 12: Solve for what you want

The desired value from the outset of this scenario is the concentration of species A at the impermeable boundary face after an elapsed amount of time, i.e. the unsteady-state concentration profile. The concentration profile produced through the solution of the differential equation is evaluated at the impermeable boundary location; this can be deduced graphically from the right hand side of Figure 5.

CONCENTRATION-DEPENDENT DIFFUSION COEFFICIENT

This problem takes the previous scenario of unsteady-state diffusion in a plane sheet with an impermeable boundary and makes the diffusion coefficient concentration-dependent, e.g. $D_{AB} = f(c_A)$, instead of a constant. This changes the constitutive equation for species flux in Step 4 to $N_A = f(c_A)\frac{\partial c_A}{\partial z}$. When this is combined with the shell mass balance while forming the differential equation in Step 6, the result is

$$\frac{\partial^2 c_A}{\partial z^2} + \frac{1}{f(c_A)}\frac{\partial f(c_A)}{\partial c_A}\left(\frac{\partial c_A}{\partial z}\right)^2 - \frac{1}{f(c_A)}\frac{\partial c_A}{\partial t} = 0$$

a second-order quasilinear homogeneous partial differential equation with variable coefficients. Reference searching for a worked through solution did not find any readily available; those that were found were for infinite and semi-infinite media (5). Time did not allow for further work on this problem, but numerical methods are the likely path to success (24).

HETEROGENEOUS MATERIALS

One scenario of diffusion in heterogeneous materials is discussed in the following chapter and concerns primarily impermeable platelet filler material. Barrer's

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chapter §6 in (15) deals extensively with the subject of diffusion in heterogeneous media, including models for layers of laminate sheets, dispersions of various geometries of one phase within a bulk phase, and filled rubbers. Regarding laminates, the author here makes the point that the full solution of the diffusion equation in each layer may not be practical, but that there exist methods to gain useful insight without the complete solution. A mention of diffusion in a flake-filled film can be found in (1). Decker et al. take advantage of different polymer-polymer diffusion rates when creating a multilayer barrier polymer film loaded with oriented nanoclay platelets (54) (see Chapter 5).

OTHER RELEVANT PROBLEMS

One common diffusion measurement technique is by recording the mass uptake of penetrant by a polymer sample disk. The established equations for interpreting the mass change data assume a negligible dimensional change due to entrained penetrant. It is especially important that the thickness not change as it factors significantly in the diffusion coefficient calculation. This invariance may not be the case if significant penetrant uptake occurs and swells the polymer disk. Fortunately, there is guidance for interpreting data from such an occurrence that can be found in §10.6.5 of (5).

Another diffusion problem of marine hardware relevance is that of leaching. Desorption of volatile or otherwise mobile material components can change material properties such as glass transition temperature, stiffness, and sound speed. In some cases it may be desired to lose a penetrant over time, such as an anti-fouling biocide or entrained water (e.g. drying out hardware). The boundary conditions associated with leaching phenomena may be different from the scenarios mentioned before. For

example, the penetrant diffusivity in the polymer may be high such that a slow surface

removal (modeled by an interphase mass transfer equation) controls the rate of penetrant

loss.

CHAPTER 5: BARRIER POLYMER APPLICATION

This section is included to illustrate some complexities of real-world transport applications and connect their origins to the fundamental steps of the flowchart tool.

Introduction

The goals of a barrier polymer are to minimize permeation while being minimally present. Permeation should be a non-issue for the effective service life of the product it is protecting and should not dictate the thickness of coatings. At the same time, any barrier additive or structural content should be minimized and not adversely alter the production process, i.e. be a 'facile' process (55). Nano-composite platelet additives offer a solution to this problem, achieving dramatic improvement in permeation reduction with minimal loading; it is expected this can be further enhanced by ensuring the platelets are properly oriented (56).

Barrier mechanism

The primary mechanism by which platelets and polymer crystals retard small molecule permeation is tortuosity (56) (57) (58). The additive itself being near-impermeable (especially relative to the polymer), the small molecule is forced to diffuse around the structure. This effectively increases the 'thickness' of the coating as permeating molecules must travel a longer overall path through the polymer. A high aspect ratio enhances this mechanism by maximizing the size of the obstacle the molecule must circumnavigate while minimizing thickness, and thereby weight. A cartoon of this mechanism is shown in Figure 6.
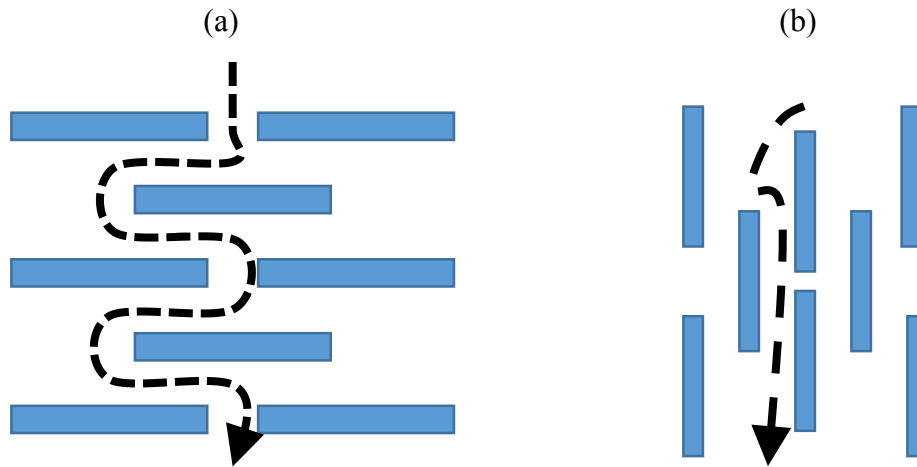
Figure 6 Tortuosity cartoon illustrating diffusion (a) normal to platelet orientation, and (b) parallel to platelet orientation.

Figure 6-a is an idealized cartoon of barrier platelets forcing a permeating molecule to travel a twisted, tortuous path through the polymer. If properly oriented like this, the platelets act like shingles on a roof (56). Care should be taken to ensure that diffusion parallel to platelet orientation is not a problem, as illustrated in Figure 6-b. This extreme alignment may not be as effective a barrier in the transverse direction. A random orientation may not have the optimal barrier property as in Figure 6-a, but it is more likely to provide a decent barrier in all directions.

Permeation Prediction

Platelet polymer additives and polymer crystals reduce the permeation rate of small molecules through the bulk polymer. Although qualitatively understood, the accurate quantitative prediction of this reduction is a challenging problem. Barrer's chapter in (15) deals extensively with the subject of diffusion in heterogeneous media. Mittal (59) reviewed common models for polymer nano-composites and found they

lacked an accounting for specific nonidealities, namely the scenarios of incomplete exfoliation of platelet particles and mis-aligned sheets. The Nielsen model

$$\frac{P_c}{P_m} = \frac{1-\phi_f}{1+\frac{\chi}{2}}$$

$$\chi = \alpha\phi_f$$

models a regular array of polymer additive 'ribbons' of infinite length (57). The Cussler & Aris et al. model

$$\frac{P_c}{P_m} = \frac{1}{1+\mu\chi^2}$$

$$\mu = \frac{\pi^2}{\left(8\ln(^\alpha/_2)\right)^2}$$

models a random array of aligned flakes or lamellae (60). P_c and P_m refer to the permeability coefficients of the composite material and the pure polymer, respectively.

Mittal argues that using factorial design methods to include these nonideal behaviors in the model accounts for experimentally observed behaviors such as the reduction in barrier performance when the polymer is saturated with nano-platelets at a particular filler fraction (Φ_f). Properties such as platelet aspect ratio (α) and percent randomness can be calculated from experimental permeation behavior and filler volume fraction.

These models were derived with the underlying assumption of ideal Fickian diffusion behavior, such that the permeability coefficient is the product of the diffusion coefficient and solubility. In the scope of the flowchart tool, these models took step 4 and added terms to the constitutive equation for species flux to account for the increased resistance to flow due to the dimensional tortuosity of the added platelet flakes.

Platelet Barriers

Conventional types of platelets include mica and talc (61). These materials have a diameter of 10-1000 μm and are around 1-5 μm thick, which gives them a surface-area to volume ratio (A/V) of ~$6x10^5$ m^{-1}. By comparison, well-exfoliated phyllosilicate sheets e.g. montmorillonite (MMT) or kaolinite (KT) can have diameters of 8-10 μm and thickness down to 1 nm, giving an A/V ratio of ~$2x10^9$ m^{-1} (~3000x greater) (56). Assuming a platelet is a solid cylinder of diameter *d* and thickness *t*, the equation for surface-area to volume ratio is:

$$\frac{A}{V} = \frac{2\left(\pi d^2/4\right) + t\left(2\pi d/2\right)}{t\left(\pi d^2/4\right)} = \frac{2(d+2t)}{td}$$

The larger A/V ratio means more surface area for adhesion of the nano-platelet to the polymer is available for less volume of filler added, and that more barrier influence can occur with lower loading of additive. This exfoliation typically requires chemical assistance through treatment with organophillic cationic surfactants (e.g. alkyl ammonium salts) (56) or sonication (62). Shear from processing also promotes exfoliation of the sheets, and it is worth noting at this time the different regimes that can be expected of nano-platelet additives in polymers: segregated, exfoliated, and intercalated.

Segregated implies virtually no dispersion, more like a two-phase system. Exfoliated describes platelet sheets that are well removed from one another. Intercalated describes separate sheets that are relatively close to each other, less than the order of the platelet diameter. In this case, single polymer chains wind their way between sheets in the space referred to as the 'gallery' (56).

Platelet Orientation & Polymer Processing

It has been noted (54) that dilute concentrations of nano-clay sheets provide some tortuosity and restrict permeation, but semi-dilute concentrations amplify the effect through multiple scatterings of the penetrant molecules between the less-disperse sheets. One difficulty in processing is that higher concentrations of additives increase the polymer melt viscosity such that the material cannot be extruded. The conundrum is therefore a limit on barrier additive loading level due to processing considerations. One clever approach that gets around this problem is the use of multilayer co-extrusion with post-processing annealing (54).

In multilayer co-extrusion, two feed streams are fed through a series of layer multiplying elements which split, spread, and recombine the streams. The result is an extruded product with any number of alternating layers of material. In Decker et al. (54) this method was used to prepare alternating layers of low-density polyethylene (LDPE) with linear-low-density polyethylene (LLDPE) loaded with MMT nanoclay at a low concentration so as not to interfere with the extrusion process.

During the annealing phase, polymer-polymer interdiffusion of the LDPE and LLDPE resulted in a 'moving-front' of the phase boundary due to the different molecular mobilities of the two polymers. The result was a compaction of the clay-loaded layer and an expansion of the other. The end result is regions of high nano-platelet additive providing enhanced barrier properties. The feat worth noting is that this was achieved without initially high loading that would make processing the polymer by extrusion nigh-impossible.

Platelet orientation can also be influenced by other mechanisms, not just shearing forces in extrusion-type flow. Yucel et al. (62) describe a multilayer solution casting method which results in platelet orientation as the solvent evaporates. The polymer chains collapse as the solvent leaves, compacting the remaining polymer and nano-clay. Large internal stresses from this behavior resulted in bending of the nano-clay at high loading.

Platelets and Polymer Crystals

In addition to acting as barriers, platelet additives can also serve as nucleation sites for polymer crystals. This behavior was described in Girdthep et al. and was cited as the reason for enhanced strength in an unexpected orientation of the final product (63).

After melt blending PLA (poly-lactic acid), PBAT (poly-butylene-adipate-co-terephthalate), the combatibilizer TBT (tetrabutyl titanate), and kaolinite with silver; the result was processed through blown film extrusion. The researchers found extended and oriented polymer chains in the machine direction (MD), but also found crystal growth from the clay platelets in the transverse direction (TD). They reported that subsequent tensile testing revealed greater strength in the TD orientation than the MD orientation for the nano-composite sample. However, the data referred to in the article did not obviously corroborate the reported results.

Work done by Chatterjee et al. (64) described the barrier ability and influence of processing on polymer crystals without additives. An interesting result was the existence of a critical draw ratio, below which polymer processing and orientation of crystals actually *increases* permeation rate.

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Forming high-density polyethylene (HDPE) through a blown film process followed by machine direction orientation processing resulted in three different polymer crystal structures, each with different barrier properties. The HDPE from the blown film contained random, spherulite crystals which lent a degree of tortuosity to the polymer. At low draw ratios, the crystals organized into a lamellar structure in the machine direction; this effectively decreased tortuosity and increased measured permeation rates. After a certain point (the 'critical draw ratio') the lamellar crystals transform to a microfibrillar zig-zag pattern with smaller crystals developing around the fibers. This decreased the amorphous fraction and, along with the increased orientation, resulted in significant reduction of permeation rate.

CHAPTER 6: SUMMARY AND OUTLOOK

Through the course of this research a flowchart process tool was developed to guide chemical and non-chemical engineers in the solution of polymer-penetrant diffusion problems, with a focus on those scenarios expected for marine hardware. The tool incorporates references to databanks and experimental methods that will produce values for the parameters in the equations developed through the flowchart process tool, assisting users in achieving numerical answers to their practical problems. The development of the flowchart process tool was influenced and demonstrated by applying it to solve example diffusion problems which also had marine hardware relevance. Literature on the barrier character of nanoclay platelet fillers in polymers was reviewed, demonstrating a promising current technology and the complexity of real-world applications. The modeling of resulting increase in permeation time was connected with the appropriate step in the flowchart tool.

The results of this effort are already bearing fruit for the author, as he is using the flowchart process tool to tackle the anti-fouling biocide leaching problem mentioned earlier in the text. Further refinement of the flowchart tool is expected as it continues to be used in this manner.

This body of work is anticipated to be a foundation for future guidance documentation for marine hardware designers to assist them in material selection decisions and avoid diffusion-related problems. Initial dissemination is expected to be to acoustic hardware engineers.

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APPENDIX 1:

MARINE-HARDWARE-RELEVANT DIFFUSION PROBLEM

QUESTIONS

- How long [time] until [concentration] at [position]?
  - This would be the concentration profile, solved for time. An example situation could be a criteria for failure where an electrical property of the bulk material reaches an unacceptable value at a specific value of concentration of penetrant.

- How long [time] until [flux] becomes [value] at [position]?
  - Flux equation (function of concentration, therefore position and time), solved for [time].

- How long [time] until [amount] moves through a coating?
  - Integrate flux equation, at coating surface [position], solve for [time].

- What material do I need [diffusion coefficient] so it lasts [criteria, e.g. specified concentration(x,t)] [time]?
  - Specify length (thickness)
  - [criteria] = concentration, Concentration profile, solve for [diffusion coefficient].
  - [criteria] = flux, Flux equation, solve for [diffusion coefficient].

- What alternate material should I use with lower D_{AB}?
  - Acceptable ranges based on factors, e.g. thickness, solubility…

- What alternate thickness do I need, or what thickness do I need based on anticipated D_{AB} of my material?
- Can I put another layer of material with lower D_{AB} on top to fix the problem? How thick does it need to be?
- How long will it last (what is the maximum contact time)?
- How long will it take to dry out?
- How to handle exotic diffusion mechanisms, e.g. nanoclay tortuosity?
- How long will it last (losing & reacting anti-oxidant, losing biocide)?
- What initial loading should I use to get my desired service life? (solubility upper limit, leaching biocide).

APPENDIX 2:

MARINE-HARDWARE-RELEVANT DIFFUSION PROBLEM

GEOMETRIES

- Plane sheet

  o Example: a transducer's acoustic window.

- Impermeable boundary

  o Example: a polymer encapsulant coating on a metal component.

- Plane sheets in series (layers)

  o Example: composite laminates (e.g. fiberglass).

- Cylindrical

  o Example: the hose of a towed array.

APPENDIX 3:

MARINE-HARDWARE-RELEVANT DIFFUSION PROBLEM

INITIAL & BOUNDARY CONDITIONS

- Anticipated Marine-Hardware-Relevant Boundary Conditions:
    - Concentration is zero at ocean surface
        - (infinite sink, no diffusive resistance layer)
    - Impermeable boundary at interior
        - (metal or component underneath coating)
    - Concentration is a function of time
        - (unsteady-state interface between layers)
        - Concentration is a function of time and is in equilibrium with exterior/interior phase
            - (unsteady-state interface between layers)
    - Concentration is at solubility limit at ocean surface
        - (water permeation)
    - Concentration is in equilibrium with exterior concentration at outer surface
        - (drying out in a low-humidity environment; absorption of component dissolved in exterior phase, e.g. oxygen)

- Anticipated Marine-Hardware-Relevant Initial Conditions:
    - Initial concentration is zero everywhere
        - (starting free of species A)
    - Initial concentration is constant everywhere
        - (starting from saturation or initial loading of species A)
    - Initial concentration is a function of position
        - (starting from a system already in progress, e.g. drying, biocide leaching)

APPENDIX 4:

DIFFERENTIAL EQUATION SOLUTION METHOD APPLICABILITY CHART

Method name	Source	PDE	nth order	Nonlinear	Non-homogeneous	Coefficients variable
integrating factor	(23)	N	N	N	Y	Y
characteristic equation	(23)	N	Y	N	N	N
undetermined coefficients	(23)	N	Y	N	Y	N
variation of parameters	(23)	N	Y	N	Y	N
Separation of variables	(19)	Y	Y	N	N	Y
Laplace transform [0,∞)	(19)	Y	Y	N	Y	N
Euler, Runge-Kutta	(24)	N	Y	Y	Y	Y
Shooting, collocation	(24)	N	Y	Y	Y	Y
Finite difference	(24)	Y	Y	Y	Y	Y

Table 6 Solution method applicability, differential equation characteristics

Method name	Source	BC Nonlinear	BC Non-homo-geneous	Initial condition dis-continuous?	Initial or Boundary Value Problem?	Independent variable region restriction?
integrating factor	(23)					
characteristic equation	(23)					
undetermined coefficients	(23)					
variation of parameters	(23)					
Separation of variables	(19)	N	N			
Laplace transform [0, ∞)	(19)	Y	Y			Y
Euler, Runge-Kutta	(24)	Y	Y		Initial	
Shooting, collocation	(24)	Y	Y		Boundary	
Finite difference	(24)	Y	Y			

Table 7 Solution method applicability, boundary condition characteristics

UNSTEADY-STATE DIFFUSION PROBLEM WORK,

UP TO CHOOSING A SOLUTION METHOD.

*Note: the step numbers here predate the final numbered steps presented in the

chapter 2 flowchart description. Expect some discrepancy.

FORM THE PROBLEM:

1. Clearly define the desired solution
    - What will the molar concentration of species A be in the coating at the wall after time *t* has elapsed if the material is initially devoid of A?
        - Looking for concentration (c_A) at a particular position as a function of time, unsteady concentration profile.
2. Draw picture(s)

z=0   z = L
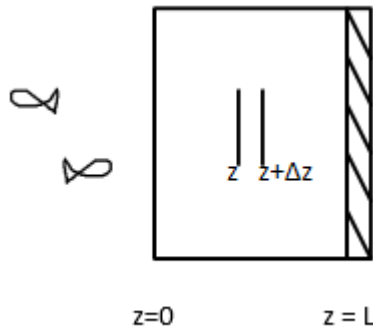
    - The z axis goes from left to right as that is the anticipated direction of flow (high to low concentration).
3. Roughly define boundary conditions.
    - Initially the coating has zero concentration of species A.
    - After immersion, the concentration of A just inside the surface immediately reaches equilibrium with the exterior environment and remains at that value the entire time it is immersed.
    - No species A leaves the coating at the coating-metal surface, i.e. the flux of A in the positive z direction is zero at z = 0
    - At large times, the concentration throughout the coating will be uniform and equal to the concentration of A in equilibrium with the exterior environment.
4. Put what you want to know in terms of the flux or other transport property.
    - $c_A|_{z=L} = f(z,t)$
    - Since the question is concerned with finding the time required to achieve a specific concentration at a specific position, what you want to know is simply an algebraic re-arrangement or simple iterative solution (Newton's method, Goalseek in Excel) of the concentration profile. Since this is developed by 'solving' the differential equations formed in this process, no additional equations are necessary.

5. Define the constitutive equation for species flux.
  - From BSL2007Trans Table 17.8-2 eqn. B
    - $J_{Az}^* = -cD_{AB}\frac{dx_A}{dz}$
    - J^*_{Az} is the molar flux of species A in the positive z direction.
    - c is the molar density, i.e. total moles per unit volume [=] total moles / volume
    - D_{AB} is the diffusivity of species A through coating B [=] area/time
    - x_A is the mole fraction of species A [=] $moles_A$ / total moles
    - z is the length axis [=] length
  - The bulk coating material B is stationary so there is no convective term expected. Conduct a shell mass balance.
  - For the thin shell volume indicated in the drawn picture:
    - (Rate of moles of species A...)(In - Out + Generation - Consumption) = Rate of accumulation or loss of moles of A in the volume.
    - $SJ_{Az}^*|_z - SJ_{Az}^*|_{z+\Delta z} + 0 - 0 = S\Delta z\frac{dc_A}{dt}$
    - S is the surface area of the z-normal face of the unit volume [=] area.
    - c_A is the molar concentration of species A [=] $moles_A$ / volume.
    - No generation or consumption term as there is no chemical reaction within the bounded region.
    - We expect an accumulation term since the coating is initially free everywhere of species A, so a change in concentration with time term makes sense; the system is not at steady-state.
    - So:
    - $SJ_{Az}^*|_z - SJ_{Az}^*|_{z+\Delta z} = S\Delta z\frac{dc_A}{dt}$
    - Dividing by SΔz and taking the limit as Δz goes to zero:
    - $-\frac{\partial J_{Az}^*}{\partial z} = \frac{\partial c_A}{\partial t}$

Insert the constitutive equation for flux into the shell mass balance result.
  - Constitutive flux equation:
    - $J_{Az}^* = -cD_{AB}\frac{dx_A}{dz}$
  - Shell mass balance result:
    - $-\frac{\partial J_{Az}^*}{\partial z} = \frac{\partial c_A}{\partial t}$
  - Combined:
    - $-\frac{\partial}{\partial z}\left(-cD_{AB}\frac{\partial x_A}{\partial z}\right) = \frac{\partial c_A}{\partial t}$
    - Simplifying for constant diffusivity within the coating and re-arranging to match units:
    - $D_{AB}\frac{\partial}{\partial z}\left(\frac{\partial c_A}{\partial z}\right) = \frac{\partial c_A}{\partial t}$
  - Re-written for differential equation analysis:
    - $D_{AB}\frac{\partial^2 c_A}{\partial z^2} = \frac{\partial c_A}{\partial t}$

Re-define boundary conditions based on the parameters in the differential equation.
  - I.C.1: at t = 0, all z, $c_A = 0$
  - B.C.1: for t > 0, z = 0, $c_A = c_{A0}$
  - B.C.2: for t > 0, z = L, $J^*_{Az} = 0$
  - F.C.1(final condition): for t >> 0, all z, $c_A = c_{A0}$

IDENTIFY THE MATH AND SELECT A SOLUTION METHOD:

9. Identify the type of differential equation produced by combining the shell mass balance and constitutive equation for species flux developed earlier.
   - $\frac{\partial c_A}{\partial t} = D_{AB} \frac{\partial^2 c_A}{\partial z^2}$
   - Order: 2nd
   - Number of independent variables: 2, partial differential equation
   - Linearity: linear
   - Homogeneity: homogeneous
   - Coefficients: constant
   - Basic type:
     - General form (Farlow1993PDE§41p.331 notation)
       - $Au_{zz} - Eu_t = 0$
       - $B^2 - 4AC = (0)^2 - 4(1)(0) = 0$
     - => Parabolic
   - Bounds of the independent variables:
     - $0 \leq z \leq L$
     - $0 \leq t < \infty$
10. Identify the types of boundary and initial conditions.
    - I.C.1: at t = 0, all z, $c_A = 0$
    - B.C.1: for t > 0, z = 0, $c_A = c_{A0}$
      - Dependent variable (c_{A0}) specified at the boundary.
      - => Type 1 (Farlow)
      - Nonhomogeneous linear.
    - B.C.2: for t > 0, z = L, $J^*_{Az} = 0$ (i.e. $\partial c_A/\partial x = 0$)
      - Flux is specified at the boundary, impermeable surface.
      - => Type 3 (Farlow1993PDE§3p.23)
      - Homogeneous linear.
    - F.C.1(final condition?): for t >> 0, all z, $c_A = c_{A0}$

UNSTEADY-STATE DIFFUSION PROBLEM WORK,

SEPARATION OF VARIABLES METHOD

APPLY THE SOLUTION METHOD AND SOLVE FOR WHAT YOU WANT:

12. Apply the solution method: separation of variables
    a. Transform nonhomogeneous boundary conditions into homogeneous ones
       (Farlow1993PDE§6p.44)
       - PITFALL AVOIDANCE: non-dimensionalize early so math tricks like orthogonality
         can be used. Example: non-dimensionalize physical boundaries so space region
         varies between 0 and 1 as opposed to 0 to L.
       - Think about the steady-state solution
         - As t -> ∞, what will the concentration profile look like?
         - Answer: uniform everywhere at c_{A0}
       - Form the final equation as the linear combination of two terms: a steady-state part
         and a transient part (which will go to zero as t -> ∞).
         - Using Farlow's notation, with u = c_A; x = z:
         - u(x,t) = steady + transient
         - u(x,t) = c_{A0} + U(x,t)
       - Substitute this new relationship into what has been defined for PDE, BCs, & IC &
         solve for the transient part [U(x,t)]
         - PDE (for $0 \leq x \leq L$; $0 < t < \infty$)
           - $u_t = D_{AB} u_{xx}$
           - $\frac{\partial}{\partial t}[c_{A0} + U(x,t)] = D_{AB}\frac{\partial^2}{\partial x^2}[c_{A0} + U(x,t)]$
           - $U_t = D_{AB} U_{xx}$
         - BCs (for $0 < t < \infty$)
           - u(0,t) = c_{A0}
             - $c_{A0} + U(0,t) = c_{A0}$
             - $U(0,t) = 0$
           - u_x(L,t) = 0
             - $\frac{d}{dx}[c_{A0} + U(L,t)] = 0$
             - $U_x(L,t) = 0$
         - IC (for $0 \leq x \leq L$)
           - u(x,0) = 0
           - $c_{A0} + U(x,0) = 0$
           - $U(x,0) = -c_{A0}$
       - Now, the transformed problem has become:
         - PDE (for $0 \leq x \leq L$; $0 < t < \infty$)
           - $U_t = D_{AB} U_{xx}$
         - BCs (for $0 < t < \infty$)
           - $U(0,t) = 0$
           - $U_x(L,t) = 0$
         - IC (for $0 \leq x \leq L$)
           - $U(x,0) = -c_{A0}$

- ▪ … which is solvable by separation of variables. The result U(x,t) is then re-introduced to the original problem, u(x,t) = c_{A0} + U(x,t).

  Changing notation to match our problem:
- ▪ u(x,t) = c_{A0} + U(x,t)
- ▪ … becomes
- ▪ c_A(z,t) = c_{A0} + γ(z,t)

  Also, non-dimensionalize the space variable z so the range of the problem goes from 0 to 1:
- ▪ $\zeta = \frac{z}{L}$

  For $0 \le z \le L$, $0 \le \zeta \le 1$

  The final problem ready for solution by separation of variables is therefore:
- ▪ PDE (for $0 \le \zeta \le 1$; $0 < t < \infty$)
  - • $\gamma_t = D_{AB}\gamma_{\zeta\zeta}$
  - • Note: $D_{AB} = D_{AB}/L^2$ from this point forward in the derivation.
- ▪ BCs (for $0 < t < \infty$)
  - • $\gamma(0,t) = 0$
  - • $\gamma_\zeta(1,t) = 0$
- ▪ IC (for $0 \le \zeta \le 1$)
  - • $\gamma(\zeta,0) = -c_{A0}$

b. Separation of variables:
  i. Step 1: form the elementary solutions which satisfy the PDE.
  - ▪ Done previously in ([Farlow1993PDE§5](#))
  - ▪ $\gamma(\zeta,t) = e^{-\lambda^2 D_{AB}t}[A\sin(\lambda\zeta) + B\cos(\lambda\zeta)]$
  - ▪ … perhaps verify that this indeed describes the PDE…
  ii. Step 2: form the fundamental solutions which satisfy the PDE and BCs.
  - ▪ Apply the boundary conditions to solve for constants of integration.
  - ▪ B.C.1: $\gamma(0,t) = 0$ => B = 0
  - ▪ B.C.2: $\gamma_\zeta(1,t) = 0$
    - • $\frac{d}{d\zeta}[Ae^{-\lambda^2 D_{AB}t}\sin(\lambda 1)] = 0$
    - • $A\lambda e^{-\lambda^2 D_{AB}t}\cos(\lambda) = 0$
    - • … λ cannot be 0 (trivial solution), neither can the exponential become zero. Therefore:
    - • $\cos(\lambda) = 0$
    - • $\lambda_n = \pm\frac{(2n-1)\pi}{2}$
      - • … where n = 1,2,3,…
  - ▪ Finally,
    - • $\gamma_n(\zeta,t) = e^{-\lambda_n^2 D_{AB}t}\sin(\lambda_n\zeta)$
    - • $\gamma_n(\zeta,t) = e^{-\left(\frac{(2n-1)\pi}{2}\right)^2 D_{AB}t}\sin\left(\frac{(2n-1)\pi}{2}\zeta\right)$
    - • … perhaps verify that this indeed describes the PDE and both BCs…
  iii. Step 3: form the final solution which satisfies the PDE, BCs, and IC.
  - ▪ Linear combination of solutions:
    - • $\gamma(\zeta,t) = \sum_{n=1}^{\infty}\left[A_n e^{-\lambda_n^2 D_{AB}t}\sin(\lambda_n\zeta)\right]$
  - ▪ Apply the initial condition (IC).
    - • IC

- $\gamma(\zeta, 0) = -c_{A0}$
- $-c_{A0} = \sum_{n=1}^{\infty}\left[A_n e^{-\lambda_n{}^2 D_{AB}(0)} \sin(\lambda_n \zeta)\right]$
- $-c_{A0} = \sum_{n=1}^{\infty}[A_n \sin(\lambda_n \zeta)]$

- Solve for the coefficients A_n
  - Orthogonality to reduce terms: multiply both sides by $\sin(\lambda_m \zeta)$ and integrate from 0 to 1.
  - $-c_{A0} \sin(\lambda_m \zeta) = \sin(\lambda_m \zeta) \sum_{n=1}^{\infty}[A_n \sin(\lambda_n \zeta)]$
  - $-c_{A0} \int_0^1 \sin(\lambda_m \zeta) d\zeta = \int_0^1 A_1 \sin(\lambda_1 \zeta) \sin(\lambda_m \zeta)\, d\zeta +$
    $\int_0^1 A_2 \sin(\lambda_2 \zeta) \sin(\lambda_m \zeta)\, d\zeta + \cdots + \int_0^1 A_m \sin(\lambda_m \zeta) \sin(\lambda_m \zeta)\, d\zeta + \cdots$
    - ... all terms where n ≠ m become zero due to orthogonality.
  - $-c_{A0} \int_0^1 \sin(\lambda_m \zeta) d\zeta = A_m \int_0^1 \sin^2(\lambda_m \zeta)\, d\zeta$
  - $-c_{A0} \frac{-1}{\lambda_m}[\cos \lambda_m - 1] = A_m \frac{1}{\lambda_m}\left[\frac{1}{2} - \frac{\sin(2\lambda_m)}{4}\right]$
  - $c_{A0}[\cos \lambda_m - 1] = A_m \left[\frac{1}{2} - \frac{2\sin(\lambda_m)\cos(\lambda_m)}{4}\right]$
  - $c_{A0}[\cos \lambda_m - 1] = A_m \frac{1 - \sin(\lambda_m)\cos(\lambda_m)}{2}$
  - $A_m = \frac{2c_{A0}[\cos \lambda_m - 1]}{1 - \sin \lambda_m \cos \lambda_m}$
    - ... since n = m:
  - $A_n = \frac{2c_{A0}[\cos \lambda_n - 1]}{1 - \sin \lambda_n \cos \lambda_n}$
    - Recall the definition of λ_n:
      - $\lambda_n = \pm \frac{(2n-1)\pi}{2}$
    - This makes all $\cos(\lambda_n)$ terms equal to zero for all n = 1, 2, 3, …
    - ... as well as all $\sin(\lambda_n)$ terms equal to 1.
  - $A_n = \frac{2c_{A0}[(0) - 1]}{1 - (1)(0)}$
  - $A_n = -2c_{A0}$

- Plug back into the linear combination of fundamental solutions:
  - $\gamma(\zeta, t) = \sum_{n=1}^{\infty}\left[A_n e^{-\lambda_n{}^2 D_{AB} t} \sin(\lambda_n \zeta)\right]$
  - $A_n = -2c_{A0}$
  - Therefore:
  - $\gamma(\zeta, t) = \sum_{n=1}^{\infty}\left[-2c_{A0} e^{-\lambda_n{}^2 D_{AB} t} \sin(\lambda_n \zeta)\right]$
  - $\gamma(\zeta, t) = -2c_{A0} \sum_{n=1}^{\infty}\left[e^{-\lambda_n{}^2 D_{AB} t} \sin(\lambda_n \zeta)\right]$

iv. This is the end result of the method of separation of variables for finding the solution to the *transient* component of the final solution:
  - $\gamma(\zeta, t) = -2c_{A0} \sum_{n=1}^{\infty}\left[e^{-\lambda_n{}^2 D_{AB} t} \sin(\lambda_n \zeta)\right]$
    - $\lambda_n = \pm \frac{(2n-1)\pi}{2}$

c. Reconcile transformations to return to the variables of the original problem.
  i. Recall the final solution, composed of steady-state and transient components:
    - $c_A(\zeta, t) = c_{A0} + \gamma(\zeta, t)$
  ii. Insert the solution for the transient component:
    - $c_A(\zeta, t) = c_{A0} + -2c_{A0} \sum_{n=1}^{\infty}\left[e^{-\lambda_n{}^2 D_{AB} t} \sin(\lambda_n \zeta)\right]$

- $c_A(\zeta, t) = c_{A0}\left(1 - 2\sum_{n=1}^{\infty}\left[e^{-\lambda_n^2 D_{AB}t}\sin(\lambda_n\zeta)\right]\right)$
  - $\lambda_n = \pm\frac{(2n-1)\pi}{2}$
  - $\zeta = \frac{z}{L}$
- $c_A\left(\frac{z}{L}, t\right) = c_{A0}\left(1 - 2\sum_{n=1}^{\infty}\left[e^{-\lambda_n^2 D_{AB}t}\sin\left(\lambda_n\frac{z}{L}\right)\right]\right)$
- $c_A\left(\frac{z}{L}, t\right) = c_{A0}\left(1 - 2\sum_{n=1}^{\infty}\left[e^{-\left(\frac{(2n-1)\pi}{2}\right)^2 D_{AB}t}\sin\left(\frac{(2n-1)\pi}{2}\frac{z}{L}\right)\right]\right)$

13. Verify the final solution satisfies the PDE, BCs, IC, and steady-state.
    a. Separation of Variables
       i. PDE
          - $\frac{\partial c_A}{\partial t} = D_{AB}\frac{\partial^2 c_A}{\partial z^2}$
          - UPDATE: when doing derivatives, it is convenient keep z transformed as $\zeta = z/L$, because the diffusion coefficient then includes the L^{-2} feature.
          - $\frac{\partial c_A}{\partial t} = D_{AB}\frac{\partial^2 c_A}{\partial \zeta^2}$
            - $\frac{\partial}{\partial t}(c_A) = 2c_{A0}D_{AB}\sum_{n=1}^{\infty}\left[\left(\frac{(2n-1)\pi}{2}\right)^2 e^{-\left(\frac{(2n-1)\pi}{2}\right)^2 D_{AB}t}\sin\left(\frac{(2n-1)\pi}{2}\zeta\right)\right]$
          - $D_{AB}\frac{\partial^2 c_A}{\partial \zeta^2} =$

            $D_{AB}\frac{\partial}{\partial \zeta}\left(-2c_{A0}\sum_{n=1}^{\infty}\left[\left(\frac{(2n-1)\pi}{2}\right)e^{-\left(\frac{(2n-1)\pi}{2}\right)^2 D_{AB}t}\cos\left(\frac{(2n-1)\pi}{2}\zeta\right)\right]\right)$
            - $D_{AB}\frac{\partial^2 c_A}{\partial \zeta^2} =$

              $2c_{A0}D_{AB}\sum_{n=1}^{\infty}\left[\left(\frac{(2n-1)\pi}{2}\right)^2 e^{-\left(\frac{(2n-1)\pi}{2}\right)^2 D_{AB}t}\sin\left(\frac{(2n-1)\pi}{2}\zeta\right)\right]$
       ii. BCs
          - B.C.1: for t > 0, ζ = 0, $c_A = c_{A0}$
            - $c_A(0, t) = c_{A0}\left(1 - 2\sum_{n=1}^{\infty}\left[e^{-\left(\frac{(2n-1)\pi}{2}\right)^2 D_{AB}t}\sin\left(\frac{(2n-1)\pi}{2}(0)\right)\right]\right)$
            - $c_A(0, t) = c_{A0}(1 - (0))$
            - $c_A(0, t) = c_{A0}$
          - B.C.2: for t > 0, ζ = 1, J^*_{Az} = 0 (i.e. $\partial c_A/\partial \zeta$ = 0)
            - $\frac{\partial}{\partial \zeta}(c_A(1, t)) =$

              $-2c_{A0}\sum_{n=1}^{\infty}\left[\left(\frac{(2n-1)\pi}{2}\right)e^{-\left(\frac{(2n-1)\pi}{2}\right)^2 D_{AB}t}\cos\left(\frac{(2n-1)\pi}{2}(1)\right)\right]$
            - $\frac{\partial}{\partial \zeta}(c_A(1, t)) = -2c_{A0}\sum_{n=1}^{\infty}[0]$
            - $\frac{\partial}{\partial \zeta}(c_A(1, t)) = 0$

<mark>iii.   IC</mark>
          - at t = 0, all ζ, c_A = 0
            - $c_A(\zeta, 0) = c_{A0}\left(1 - 2\sum_{n=1}^{\infty}\left[e^{-\left(\frac{(2n-1)\pi}{2}\right)^2 D_{AB}(0)}\sin\left(\frac{(2n-1)\pi}{2}\zeta\right)\right]\right)$
            - $c_A(\zeta, 0) = c_{A0}\left(1 - 2\sum_{n=1}^{\infty}\left[\sin\left(\frac{(2n-1)\pi}{2}\zeta\right)\right]\right)$
              - For ζ = 0, all terms 0

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- $c_A(0,0) = c_{A0}$ (satisfies B.C.1)
- For $\zeta = 1$, infinite sum averages to ½.
- $c_A(1,0) = 0$

    iv.   Steady-state
- for t -> ∞, all z, $c_A = c_{A0}$

$$c_A(\zeta, \infty) = c_{A0}\left(1 - 2\sum_{n=1}^{\infty}\left[e^{-\left(\frac{(2n-1)\pi}{2}\right)^2 D_{AB}(\infty)}\sin\left(\frac{(2n-1)\pi}{2}\zeta\right)\right]\right)$$

- $c_A(\zeta, \infty) = c_{A0}(1 - 2\sum_{n=1}^{\infty}[0])$
- $c_A(\zeta, \infty) = c_{A0}$

14. Solve for what you want
    a.   Separation of Variables
        i.   What will the molar concentration of species A be in the coating at the wall after time *t* has elapsed if the material is initially devoid of A?
- i.e. $c_A(\zeta, t)$, $\zeta = 1$ $(z = L)$, solve for various specified *t*.

$$c_A\left(\frac{(L)}{L}, t\right) = c_{A0}\left(1 - 2\sum_{n=1}^{\infty}\left[e^{-\left(\frac{(2n-1)\pi}{2}\right)^2 D_{AB}t}\sin\left(\frac{(2n-1)\pi}{2}\frac{(L)}{L}\right)\right]\right)$$

CRANK TEXT PROBLEM, LAPLACE TRANSFORM

Original problem from (5), §2.4.3

FORM THE PROBLEM

1. Define the desired solution.
   a. Get the concentration profile $c_A(x,t)$ for the system described by (Crank1975Math§2.4.3p.21) using the Laplace transform.
2. Draw a picture.
   a. Crank starts with a plane sheet of thickness 2L with surfaces maintained at a constant concentration c_{A0} and with zero initial concentration of species A throughout the sheet.
3. Bound the problem.
   a. The sheet occupies the region -L $\leq$ x $\leq$ L; resulting in symmetry around x = 0. This leads to boundary conditions:
      i. $c_A(L,t) = c_{A0}$; $0 \leq t$ (constant concentration at x = L, sheet surface)
      ii. $(c_A)_x(0,t) = 0$; $0 \leq t$ (impermeable boundary at x = 0, sheet middle)
   b. This (steps 2 & 3) results in the concentration decreasing in the <u>negative</u> x-direction, implying net flux will be <u>negative</u> in the <u>positive</u> x-direction (a.k.a. net flux will be <u>positive</u> in the <u>negative</u> x-direction).
      - [We have previously tried to craft the problem so the net flux is positive in the positive x-direction.]

Relationship between desired solution and concentration profile.

   The desired solution is the concentration profile, so no further relationship is necessary.

Define the constitutive equation for species flux.

   Fickian diffusion is assumed here, with no bulk flow or convective flux term.

$$N_{Ax} = -D_{AB}\frac{\partial c_A}{\partial x}$$

Conduct the shell mass balance.

   Unsteady-state, no reaction

$$-\frac{\partial N_{Ax}}{\partial x} = \frac{\partial c_A}{\partial t}$$

Combine equations.

$$D_{AB}\frac{\partial^2 c_A}{\partial x^2} = \frac{\partial c_A}{\partial t}$$

Boundary & Initial conditions.

   Boundary conditions

   i. $c_A(L,t) = c_{A0}$; $t \geq 0$

   ii. $\frac{\partial}{\partial x}c_A(0,t) = 0$; $t \geq 0$

   b. Initial condition

   i. $c_A(x,0) = 0$; $0 \leq x < L$

IDENTIFY THE MATH AND SELECT A SOLUTION METHOD:

9. Differential equation.
    a. From step 7,
        i. $D_{AB} \frac{\partial^2 c_A}{\partial x^2} = \frac{\partial c_A}{\partial t}$
    b. 2nd order homogeneous linear partial differential equation with constant coefficients.
    c. Type: (B² - 4AC = ?)
        i. $Au_{xx} + Bu_{xt} + Cu_{tt} + Du_x + Eu_t + Fu = G$
            1. $A = D_{AB}$
            2. $B = 0$
            3. $C = 0$
        ii. B² - 4AC = 0 ==> Parabolic
10. Boundary conditions.
    a. From step 8,
        i. $c_A(L, t) = c_{A0} \; ; t \geq 0$
            ▪ Nonhomogeneous linear.
            $\frac{\partial}{\partial x} c_A(0, t) = 0 \; ; t \geq 0$
            ▪ Homogeneous linear.
        Overall:
            Homogeneous linear: 1
            Nonhomogeneous linear: 1
    Solution method.
        The text uses the Laplace transform.

APPLY THE SOLUTION METHOD AND SOLVE FOR WHAT YOU WANT:

12. Apply the solution method (Laplace transform). (Crank1975Math§2.4.3p.21)
    a. Laplace transform the PDE & BCs
        i. PDE
            ▪ $D_{AB} \frac{\partial^2 c_A}{\partial x^2} = \frac{\partial c_A}{\partial t}$
            ▪ $\mathcal{L}\left[D_{AB} \frac{\partial^2 c_A}{\partial x^2}\right] = \mathcal{L}\left[\frac{\partial c_A}{\partial t}\right]$
                • $\mathcal{L}\left[D_{AB} \frac{\partial^2 c_A}{\partial x^2}\right]$
                    • $D_{AB}\mathcal{L}\left[\frac{\partial^2 c_A}{\partial x^2}\right]$
                    • $D_{AB} \frac{\partial^2 \bar{c}_A(x,p)}{\partial x^2}$
                    • ... (Farlow1993PDE§13p.100)
                • $\mathcal{L}\left[\frac{\partial c_A}{\partial t}\right]$
                    • $p\bar{c}_A(x,p) - c_A(x,0)$
                    • ... (Farlow1993PDE§13p.100)
                    • ...initial condition $c_A(x,0) = 0$...
                    • $p\bar{c}_A(x,p)$
            ▪ Combined:

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- $D_{AB} \frac{\partial^2 \bar{C}_A(x,p)}{\partial x^2} = p\bar{C}_A(x,p)$
- $\frac{\partial^2 \bar{C}_A(x,p)}{\partial x^2} = \frac{p}{D_{AB}} \bar{C}_A(x,p)$
- $\frac{\partial^2 \bar{C}_A(x,p)}{\partial x^2} - \frac{p}{D_{AB}} \bar{C}_A(x,p) = 0$
- ... setting $q^2 = p/D_{AB}$ (Crank1975Math§2.4.3p.22)...
- $\frac{\partial^2 \bar{C}_A(x,p)}{\partial x^2} - q^2 \bar{C}_A(x,p) = 0$

  ii. BCs

   - $c_A(L,t) = c_{A0} \; ; t \geq 0$
     - $\mathcal{L}[c_A(L,t)] = \mathcal{L}[c_{A0}]$
     - $\bar{C}_A(L,p) = \frac{c_{A0}}{p}$
   - $\frac{\partial}{\partial x} c_A(0,t) = 0 \; ; t \geq 0$
     - $\mathcal{L}\left[\frac{\partial c_A(0,t)}{\partial x}\right] = 0$
     - $\frac{\partial \bar{C}_A(0,p)}{\partial x} = 0$

b. Result:

   i. PDE

   - $\frac{\partial^2 \bar{C}_A(x,p)}{\partial x^2} - q^2 \bar{C}_A(x,p) = 0$
   - $q^2 = \frac{p}{D_{AB}}$

     BCs

   - $\bar{C}_A(L,p) = \frac{c_{A0}}{p}$
   - $\frac{\partial \bar{C}_A(0,p)}{\partial x} = 0$

c. Solve the resulting 2nd order homogeneous linear ordinary differential equation with constant coefficients (the transform variable 'p' is not considered to be variable in this case as it is not involved in the derivatives).

   i. Form the characteristic equation, determine the form of its roots, and plug back in as appropriate. ([E&P2005DiffEq§5.3](#))

   - $\frac{\partial^2 \bar{C}_A(x,p)}{\partial x^2} - q^2 \bar{C}_A(x,p) = 0$
   - Characteristic equation: Ay''+By'+Cy=0
     - A = 1
     - B = 0
     - C = -q²
   - Set $\bar{C}_A$ = y = e^{rx}
     - $r^2 e^{rx} - q^2 e^{rx} = 0$
     - $e^{rx}(r^2 - q^2) = 0$
     - ... since e^{rx} cannot be zero,
     - $r^2 - q^2 = 0$
     - $r^2 = q^2$
     - $r = \pm q = \pm\sqrt{\frac{p}{D_{AB}}}$
   - Linear combination, plug in roots for $\bar{C}_A$ = e^{rx}
     - $\bar{C}_A(x,p) = c_1 e^{qx} + c_2 e^{-qx}$
   - Solve for coefficients c_1 and c_2 using boundary conditions.
     - ... using boundary condition with the most zeros first...

- $\frac{\partial \bar{C}_A(0,p)}{\partial x} = 0$
  - PITFALL AVOIDANCE: don't forget to take the derivative when plugging-in!
- $\frac{\partial \bar{C}_A(0,p)}{\partial x} = c_1 q e^{q(0)} - c_2 q e^{-q(0)} = 0$
- $c_1 q = c_2 q$
- $c_1 = c_2$
- … changing the general solution to…
  - $\bar{C}_A(x,p) = c_1(e^{qx} + e^{-qx})$
- Second boundary condition…
  - $\bar{C}_A(L,p) = \frac{c_{A0}}{p}$
  - $\bar{C}_A(L,p) = c_1\left(e^{q(L)} + e^{-q(L)}\right) = \frac{c_{A0}}{p}$
  - $c_1 = \frac{c_{A0}}{p(e^{qL}+e^{-qL})}$
- Final form:
  - $\bar{C}_A(x,p) = \frac{c_{A0}}{p(e^{qL}+e^{-qL})}(e^{qx} + e^{-qx})$
  - … using the relation $\cosh(ax) = \frac{1}{2}(e^{ax} + e^{-ax})$
    - www.wolframalpha.com 4/7/2015
  - $\bar{C}_A(x,p) = \frac{c_{A0}\cosh(qx)}{p\cosh(qL)}$

d. Get back to the original variables (inverse transform). Crank offers two different solutions & approaches, each ultimately applicable to a different span of time for the system.

  i. Short times (small to moderate values of Dt/L²)
    - Expansion in negative exponentials…
      - $\bar{C}_A(x,p) = \frac{c_{A0}\cosh(qx)}{p\cosh(qL)} = \frac{c_{A0}(e^{qx}+e^{-qx})}{p(e^{qL}+e^{-qL})}$
      - $\bar{C}_A(x,p) = \frac{c_{A0}(e^{qx}+e^{-qx})}{pe^{qL}(1+e^{-2qL})}$
      - … binomial theorem mathemagic…
      - $\bar{C}_A(x,p) = \frac{c_{A0}}{p}\left\{e^{-q(L-x)} + e^{-q(L+x)}\right\}\sum_{n=0}^{\infty}(-1)^n e^{-2nqL}$
      - $\bar{C}_A(x,p) = \frac{c_{A0}}{p}e^{-q(L-x)}\sum_{n=0}^{\infty}(-1)^n e^{-2nqL} + \frac{c_{A0}}{p}e^{-q(L+x)}\sum_{n=0}^{\infty}(-1)^n e^{-2nqL}$
      - $\bar{C}_A(x,p) = \frac{c_{A0}}{p}\sum_{n=0}^{\infty}(-1)^n e^{-q\{(2n+1)L-x\}} + \frac{c_{A0}}{p}\sum_{n=0}^{\infty}(-1)^n e^{-q\{(2n+1)L+x\}}$
    - Inverse Laplace transform…
      - … inverse Laplace table
        - $\mathcal{L}^{-1}\left[\frac{e^{-qx}}{p}\right] = \text{erfc}\,\frac{x}{2\sqrt{D_{AB}t}}$
      - … so finally:
    - $c_A(x,t) = c_{A0}\sum_{n=0}^{\infty}\left[(-1)^n\text{erfc}\,\frac{(2n+1)L-x}{2\sqrt{D_{AB}t}}\right] + c_{A0}\sum_{n=0}^{\infty}\left[(-1)^n\text{erfc}\,\frac{(2n+1)L+x}{2\sqrt{D_{AB}t}}\right]$
      - … is the concentration profile in the half-sheet. This converges for small to moderate values of Dt/L² (i.e. 'short' times).

Concentration Profile Model
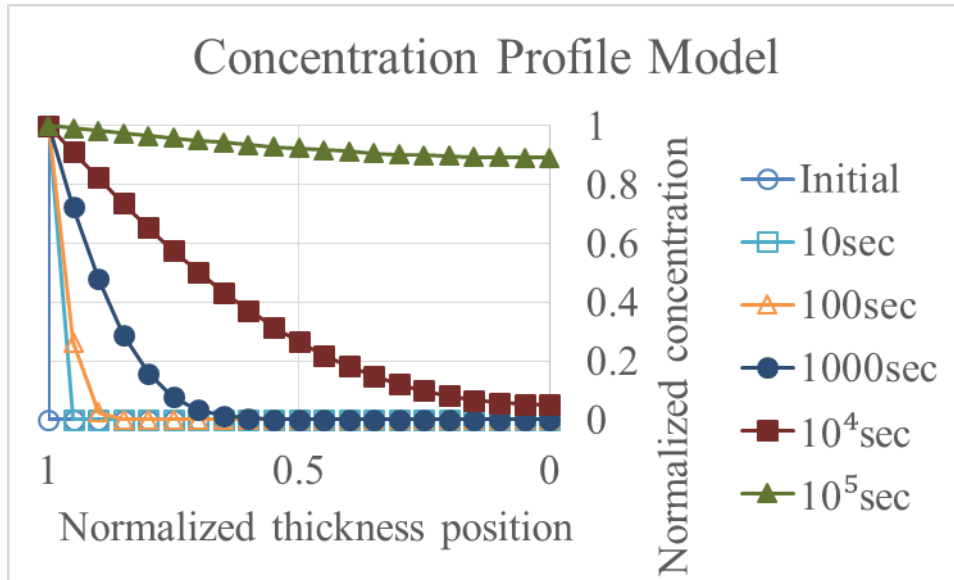
ii. Long times (large values of Dt/L^2)
- Expression in partial fractions…
  - … long derivation in text…eventually arriving at:
- $$c_A(x,t) = c_{A0} - \frac{4c_{A0}}{\pi} \sum_{n=0}^{\infty} \left[\frac{(-1)^n}{2n+1} e^{-\frac{D_{AB}(2n+1)^2 \pi^2 t}{4L^2}} \cos\left(\frac{(2n+1)\pi x}{2L}\right) \right]$$
  - … is the concentration profile in the half-sheet. This converges for moderate to large values of Dt/L^2 (i.e. 'long' times).

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