Two Illustrative Mass Transfer Problems

1. Introduction. In the first example, we will look at steady-state, one-dimensional mass transfer (i.e. mass transfer along a single direction, or coordinate axis) of a species across a film. This example is important because it is one of few problems in which diffusion-engendered convection is easily handled analytically, and is an excellent way to illustrate its effect on the total mass transfer of a species by comparing concentrated and dilute scenarios. The problem is also useful as an illustration of boundary conditions that involve heterogeneous reactions and vapor/liquid equilibria. The results from this problem form the basis of so-called "film theory" of interfacial mass transfer.

In the second problem, we will look at an unsteady-state mass transfer. The mass transfer will again occur along a single direction in space. In this problem, the species of interest will be diffusing into an infinitely wide slab of material, a so-called semi-infinite medium. The mass transfer will be under dilute conditions, so that diffusion-engendered convection will be negligible. This is an important problem because it predicts the "short-time" limit behavior for many diffusion processes. This is because, at short times after the beginning of diffusion of a species into a medium, even if the medium is finite in width the diffusion can be modeled as that into an infinitely-thick layer. Qualitatively, this approximation works because at short times the diffusing species has not yet reached the other, far interface of the layer and so its diffusion is not affected by its presence. The unsteady transfer into a semi-infinite medium will also provide opportunity to illustrate solution of partial differential equations by use of Laplace transforms.

2. Steady-State, One-Dimensional Mass Transfer with a Heterogeneous Reaction.
A container with an open top contains a gas mixture. Toward the bottom of the container, the gas solution is in contact with a solid or a liquid phase, Fig.1. For concreteness, hereafter we'll assume that this other phase is a solid. The gas-solid interface is located at \( z = z_1 \). A heterogeneous reaction occurs at this interface with the stoichiometry

\[
a \, A(g) + b \, B(g) \leftrightarrow c \, C(s) + d \, D(g)
\]

In words, \( a \) molecules of gas \( A \) react with \( b \) molecules of gas \( B \) to produce \( c \) molecules of a solid residue \( C \) and \( d \) molecules of a product gas \( D \). The gas phase in addition contains a "carrier" gas \( E \) which does not participate in the reaction. We wish to calculate the flux of species \( A \) and its concentration profile in region I, which occupies the space \( z_1 < z < z_2 \), see Fig 1.

We will work in molar units. Therefore, we will use \( y_i \) to denote the mole fraction of \( i \) in the gas phase. Following approximations and facts also apply,
(i) Reaction (1) only occurs on the surface of the solid, and not in the gas.

(ii) There is no forced or natural convection in region I, so that any bulk convection that may be present in this region is due to diffusion-engendered convection only. Under such conditions, region I is also referred to as a "diffusion zone." This assumption is justified by recognizing that the walls of the tank that confine the gas in region I also largely block its perturbation by the external crossflow present in region II (see below).

(iii) At $z > z_2$ (region II) a well mixed crossflow stream blows past the top opening of the container. The mole fractions of the various gases in this stream are $y_{A0}$, $y_{B0}$, $y_{D0}$, and $y_{E0}$. The convective exchange of the gas in region II is very rapid, so much so that mole fractions are effectively fixed at these values at all points in region II. In particular, the reaction, which consumes $A$ and $B$ and produces $D$, does not proceed at a sufficient rate to significantly alter the concentration of these species in region II from $y_{A0}$, $y_{B0}$, $y_{D0}$, and $y_{E0}$.

(iv) In region I, all species' fluxes are assumed to be one-dimensional, in the $z$-direction only. This assumption means that driving forces for diffusion parallel to the solid surface are negligible, and in particular that concentration gradients (which are one driving force for diffusion) only occur along the $z$-direction. Thus we assume that all concentrations and fluxes depend on $z$ only. At the boundary of regions I and II, this assumption is also consistent with assumption (iii), namely that the composition of the gas in region II does not vary across the opening of the container.

(v) The rate of deposition of solid $C$ is small, so that the lower boundary of region I effectively remains at $z = z_1$ throughout the process.

(vi) Steady state conditions apply.

(vii) The process is isothermal and isobaric, and ideal gas behavior holds for the gas mixture.

(viii) $D_{A \text{-mix}}$, the diffusion coefficient of $A$ through the multicomponent gas mixture, is constant for the range of mixture compositions encountered. This is consistent with assuming ideal gas behavior, in which the gas particles do not interact.

(ix) At $z = z_1$, mole fraction of species $A$ equals $y_{AS}$: $y_A(z = z_1) = y_{AS}$. 
Determine the flux and concentration profile of A in region I.

**Solution.** Many mass transfer problems are best begun by writing down the following form of the balance for species $i$:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i + R_i$$

(2)

According to assumption (i), there are no homogeneous reactions so $R_i = 0$ for all species present. Furthermore, assumption (vi) states that the process is at steady state, so that $c_i$ does not depend on time (i.e. left hand side in (2) equals 0). Therefore, (2) becomes

$$\nabla \cdot \mathbf{N}_i = 0$$

(3)

According to assumption (iv), all species' fluxes are one-dimensional, along the $z$-direction only. Then $\mathbf{N}_i = N_{iz} \mathbf{e}_z$, and equation (3) becomes

$$\nabla \cdot \mathbf{N}_i = \nabla \cdot \left( \frac{\partial}{\partial x} \delta_x + \frac{\partial}{\partial y} \delta_y + \frac{\partial}{\partial z} \delta_z \right) \cdot N_{iz} \mathbf{e}_z = \frac{dN_{iz}}{dz} = 0$$

(4)

In (4), the ordinary derivative notation is justified since by assumption $N_{iz}$ only depends on $z$. Integration of (4) leads to

$$N_{iz} = C_i$$

(5)

where $C_i$ is a constant. Thus the molar flux of each species in region I is *constant*. This result stems from the requirement that, under steady state, there can be no accumulation of $i$ at any point in region I. Then the flux of $i$ must be constant so as to ensure that the rate at which $i$ is brought to a point equals the rate at which it leaves that point.

The total molar flux is given by the sum of Fick's law and bulk convection,

$$N_{Az} = J_{Az} + c_A V_z = -c D_{A-mix} dy_A/dz + c_A V_z$$

(6)

$$N_{Az} = -c D_{A-mix} dy_A/dz + c y_A v_{Az} + y_B v_{Bz} + y_D v_{Dz} + y_E v_{Ez}$$

(7)

In writing (6), use has been made of Fick's Law, $J_{A} = -c D_{AB} \nabla y_A$. Fick's Law has been generalized to a multicomponent mixture by use of a diffusion coefficient of $A$ in the mixture, $D_{A-mix}$, instead of the binary diffusion coefficient $D_{AB}$. In writing (7), the definition of the molar average velocity $\mathbf{V}$ was employed, $\mathbf{V} = \sum_{i=1}^{n} y_i v_i$.

Since $c y_i v_{iz} = c_i v_{iz} = N_{iz}$, equation (7) becomes
According to equation (5), the flux $N_{Ez}$ of the carrier gas $E$, like that of the other species present, is constant. Furthermore, steady state requires that there be no accumulation of $E$ at the surface where the reaction takes place. Since there are no sources or sinks for $E$ at the surface ($E$ does not participate in the heterogeneous chemical reaction, and cannot diffuse into the solid $C$), there can be no net transport of $E$ to or from the surface, and $N_{Ez}(z = z_1) = 0$. Otherwise, accumulation of $E$ at the surface would result, violating steady state. The combination of the two facts, (i) $N_{Ez}(z = z_1) = 0$ and (ii) $N_{Ez}$ is constant (equation (5)), implies that

$$N_{Ez} = 0 \quad (z_1 < z < z_2) \quad (9)$$

everywhere in region I. In addition, under steady state the rate of transport of reactants and products to the reaction surface must exactly counteract their rate of production or consumption. If this were not so, accumulation of the species at the solid surface would result, violating steady state. The reaction stoichiometry is $a \ A(g) + b \ B(g) \leftrightarrow c \ C(s) + d \ D(g)$. Therefore, if a molecule of species $A$ arrives at the surface and reacts, $b/a$ molecules of species $B$ must arrive at the same time in order to react with the $A$ molecule. Therefore, we must have

$$N_{Bz} = (b/a) \ N_{Az} \quad (10)$$

Similarly, the reaction produces $d/a$ molecules of $D$ for each reacted molecule of $A$. In order not to accumulate at the surface, these reaction product molecules must be transported away in the direction opposite to the flux of the reactant species. Therefore,

$$N_{Dz} = - (d/a) \ N_{Az} \quad (11)$$

The minus sign signifies that the transport of $D$ is in a direction opposite to that of $A$.

Substitution of equations (9), (10), and (11) into (8) leads to

$$N_{Az} = -cD_{A-mix} \ \frac{dy_A}{dz} + y_A(N_{Az} + N_{Bz} + N_{Dz} + N_{Ez}) \quad (8)$$

Equation (14) is a differential equation for $y_A$. It has one integration constant in it already, the unknown flux $N_{Az}$, which resulted from the integration of the species' balance (see equation (5)). Starting from equation (5) we could have written $C_A$ instead of $N_{Az}$ to emphasize that it is an integration constant, but then its physical meaning as a molar flux would have been obscured. Equation (14) has to be integrated once more to provide an expression for $y_A$. This second integration will produce a second integration constant. Thus, two boundary conditions will be
needed to specify the two integration constants. Using the information given in assumptions (iii) and (ix), the two boundary conditions are

\[ y_A(z = z_1) = y_{AS} \]  
\[ y_A(z = z_2) = y_{A0} \]  

Integration of equation (14) is straightforward. \( N_{Az} \) is constant, \( D_{A-mix} \) is constant (assumption (viii)) and, because the gas mixture is isothermal, isobaric, and ideal (assumption (vii)) \( c = p/\rho R T \) is also constant. We note that, since ideal gas molecules do not interact with each other their distribution in space is not sensitive to composition; thus, the ideal gas assumption automatically implies that \( c \) does not depend on composition. With these considerations, equation (14) can be directly integrated,

\[ \int_{z_1}^{z_2} N_{Az} \, dz = \int_{y_{AS}}^{y_{A0}} \frac{-cD_{A-mix}}{1 - y_A(1 + b/a - d/a)} \, dy_A \]  

or

\[ N_{Az} (z_2 - z_1) = \frac{cD_{A-mix}}{(1 + b/a - d/a)} \ln \left\{ \frac{1 - y_{A0}(1 + b/a - d/a)}{1 - y_{AS}(1 + b/a - d/a)} \right\} \]  

Equation (19) is the final expression for the molar flux \( N_{Az} \). From \( N_{Az} \) the fluxes of \( B \) and \( D \) species can be calculated from equations (10) and (11), as determined by stoichiometry of the heterogeneous reaction.

In addition to the fluxes, we are also interested in the concentration profile of species \( A \) across region I, i.e. between \( z_1 \) and \( z_2 \). Integration of equation (14) from \( z_1 \) to \( z_2 \), where \( z \) is intermediate between \( z_1 \) and \( z_2 \), leads to

\[ \int_{z_1}^{z} N_{Az} \, dz = \int_{y_{AS}}^{y_A} \frac{-cD_{A-mix}}{1 - y_A(1 + b/a - d/a)} \, dy_A \]  

\( y_A \) is the mole fraction of \( A \) at \( z \). The integration in (20) is identical to that in equation (17), except for the change in the upper limit of integration where \( z \) replaced \( z_2 \) and \( y_A \) replaced \( y_{A0} \). The result is
\[ N_{Az} = \frac{cD_{A-mix}}{(z - z_1)(1 + b/a - d/a)} \ln \left\{ \frac{1 - y_A(1 + b/a - d/a)}{1 - y_{AS}(1 + b/a - d/a)} \right\} \] (21)

Setting (19) and (21) equal to each other (recall that \( N_{Az} \) is constant) and simplifying results in,

\[ \ln \left\{ \frac{1 - y_A(1 + b/a - d/a)}{1 - y_{AS}(1 + b/a - d/a)} \right\} = \frac{z - z_1}{z_2 - z_1} \ln \left\{ \frac{1 - y_{A0}(1 + b/a - d/a)}{1 - y_{AS}(1 + b/a - d/a)} \right\} \] (22)

Rearranging,

\[ \left\{ \frac{1 - y_A(1 + b/a - d/a)}{1 - y_{AS}(1 + b/a - d/a)} \right\} = \left\{ \frac{1 - y_{A0}(1 + b/a - d/a)}{1 - y_{AS}(1 + b/a - d/a)} \right\}^{(z - z_1)/(z_2 - z_1)} \] (23)

Equations (19) and (23) are the desired expressions for the flux and concentration profile of species \( A \) in region I, respectively.

**COMMENTS:**

(i) Application to liquid-gas phase equilibrium. In this situation, liquid \( A \) is at the bottom of the container, occupying the space \( z < z_1 \), Fig. 2. The liquid \( A \) evaporates to produce gas molecules of \( A \) according to the "reaction,"

\[ A(g) \leftrightarrow A(l) \] (24)

We also assume that there are no \( B \) or \( D \) species present; thus the gaseous \( A \) molecules diffuse through the inert gas \( E \). The system is therefore binary, consisting of \( A \) and \( E \) species only. We now adapt our results from above, derived for reaction (1), to this "evaporation" reaction. Reaction (1) was

![Diagram](image_url)
By inspection, we see that the evaporation reaction (24) is the same as (1) if in (1) we set

\[ a = 1, \quad b = 0, \quad c = 1, \quad d = 0 \]  

and the solid \( C \) is instead taken to be liquid \( A \). Making the substitutions (25) in equation (19) for the flux of \( A \) species leads to

\[ N_{Az} = \left( \frac{cD_{AE}}{z_2 - z_1} \right) \ln \left( \frac{1 - y_{A0}}{1 - y_{AS}} \right) \]  

In equation (26), the diffusion coefficient \( D_{A,\text{mix}} \) of \( A \) in the gas mixture was replaced by the binary diffusion coefficient of \( A \) in the gas \( E \), as these are the only two species present.

Equation (26) is therefore just a simplified form of the originally derived expression (19) for \( N_{Az} \), and therefore is subject to the same assumptions as (19), including that \( N_{Ez} = 0 \). This assumption means that for the evaporation reaction (24) \( E \) does not diffuse into the liquid \( A \). The physical picture is one in which \( A \) molecules, generated at the liquid surface by evaporation, then diffuse away (in the positive \( z \) direction) through a stagnant, stationary film of \( E \) gas.

A similar procedure can be followed to derive a formula for the concentration profile of \( A \). Substitution of the stoichiometric coefficients in (25) into expression (23) for \( y_A(z) \) leads to

\[ \left( \frac{1 - y_A}{1 - y_{AS}} \right) = \left( \frac{1 - y_{A0}}{1 - y_{AS}} \right)^{(z-z_1)/(z_2-z_1)} \]  

for the evaporation scenario. Fig. 2b plots the concentration \( y_A(z) \) for several different values of \( y_{AS} \), assuming that \( y_{A0} = 0 \). The curvature that appears at the higher concentrations (\( y_{AS} \) of 0.5 and 0.95) reflects the presence of diffusion-engendered convection. As the dilute limit is approached the concentration profile becomes linear, as evident from the \( y_{AS} = 0.1 \) curve.
(ii) Estimating the Effect of Diffusion-Engendered Convection on Flux. We will use the simple evaporation scenario presented in Comment (i) in the following illustration. The purpose is to estimate the effect of diffusion-engendered bulk convection on the flux of species $A$. More importantly, we may wish to know under what conditions is it acceptable to use a dilute limit expression, in which diffusion-engendered bulk convection is neglected, and when is it necessary to use the full expression for the flux as given in equation (26).

First, we need to derive a dilute limit formula for the flux that applies in absence of diffusion-engendered bulk convection. This is accomplished by first writing equation (26) as

$$N_{AZ} = \frac{c_{DAE}}{z_2 - z_1} \left\{ \ln(1 - y_{A0}) - \ln(1 - y_{AS}) \right\} \tag{28}$$

In the dilute limit, both $y_{A0}$ and $y_{AS}$ approach zero. In this limit, we can use the approximation

$$\ln(1 - x) \approx -x \quad \text{for} \quad x \ll 1 \tag{29}$$

Equation (29) can be proven by Taylor series expansion of $\ln(1 - x)$ around $x = 0$. Application of equation (29) to (28) under the assumption of $y_{A0}$ and $y_{AS}$ both being much less than 1 (dilute conditions) leads to

$$N_{AZ}^{Dil} = \frac{c_{DAE}}{z_2 - z_1} \left\{ -y_{A0} - (-y_{AS}) \right\} = \frac{c_{DAE}}{z_2 - z_1} (y_{AS} - y_{A0}) \tag{30}$$

$$N_{AZ}^{Dil} = \left( D_{AE} / (z_2 - z_1) \right) (c_{AS} - c_{A0}) \tag{31}$$
Instead of $N_{Az}$ we wrote $N_{Az}^{Dil}$ to emphasize the specialization to the dilute limit (note: $N_{Az}^{Dil} = J_{Az}$). Equation (31) is the desired dilute limit for the molar flux of species $A$. The expression can be shown to be the same as equation (22) in the handout on analogies between mass and heat transfer, in which one-dimensional, dilute limit diffusion of $A$ through a stagnant layer was analyzed.

The effect of diffusion-engendered bulk convection can be illustrated by taking the ratio of the full expression for the flux of $A$, equation (28), to the dilute limit expression (30),

$$N_{Az}/N_{Az}^{Dil} = \{\ln(1-y_{A0}) - \ln(1-y_{AS})\}/(y_{AS} - y_{A0})$$

(32)

If the ratio in (32) is close to one, then $N_{Az} \approx N_{Az}^{Dil}$ and dilute conditions apply, but if significant deviation from unity is observed then diffusion-engendered bulk convection cannot be neglected. We illustrate this with the following example.

**EXAMPLE.** The bottom of a vessel is filled with pure liquid benzene. The picture is the same as in Fig. 2, where species $A$ now corresponds to benzene. The benzene evaporates and then diffuses vertically up through the stagnant gas in the vessel into well mixed surroundings. Estimate the ratio $N_{Az}/N_{Az}^{Dil}$ from equation (32) at 60 °C when the vapor pressure of the liquid benzene is 37 torr, and at 60 °C when the benzene vapor pressure is 395 torr. The total pressure is 760 torr. The concentration of benzene in the surroundings can be assumed to be zero.

Denoting the benzene as species $A$, its concentration at $z = z_2$ is

$$y_{A0} = 0 \quad \text{ (no benzene is present in the surroundings, i.e. in region II)}$$

(33)

Assuming local equilibrium at the interface of the liquid benzene (at $z = z_1$),

$$y_{AS}(6 \degree C) = \rho_A/\rho_{tot} = \rho_{sat}/\rho_{tot} = 37/760 = 0.049$$

(34)

Equation (34) recognized that, at equilibrium, the partial pressure $\rho_A$ of species $A$ equals its vapor pressure $\rho_{sat}$. Similarly,

$$y_{AS}(60 \degree C) = 395/760 = 0.52$$

(35)

Inserting the values for the various mole fractions into equation (32) leads to

$$N_{Az}/N_{Az}^{Dil} (6 \degree C) = \{\ln(1-0) - \ln(1-0.049)\}/(0.049 - 0) = 1.03$$

(36)

$$N_{Az}/N_{Az}^{Dil} (60 \degree C) = \{\ln(1-0) - \ln(1-0.52)\}/(0.52 - 0) = 1.41$$

(37)

Equation (36) shows that at 6 °C, when benzene mole fraction in the vessel is dilute and less than 5 % (see equation (34)), neglecting diffusion-engendered bulk convection is an excellent assumption. Under these conditions, the total mass flux $N_{Az}$ is nearly equivalent to just the diffusion flux $N_{Az}^{Dil}$ ($= J_{Az}$), implying that bulk convection is unimportant. However, at 60 °C, the benzene mole fraction exceeds 50 % next to the liquid, and the benzene concentration in the vessel is high. As evident from equation (37), under these concentrated conditions neglecting bulk convection would underestimate the true value of the molar flux by 41 %.
(iii) Additional Applications of One-dimensional Steady Diffusion Through a Stagnant Film.

The expressions derived above, such as equation (26) for flux of species $A$, form the basis of **film theory**. Film theory models mass transfer of a species from an interface between two phases (e.g. between liquid and gas; between two liquids) into the bulk of a phase as being dominated by a resistance that arises primarily from a stagnant film near the interface. In the terminology of the prior discussion, region I would be the stagnant film and region II the well mixed bulk. The diffusing species must cross this stagnant film, and consequently the diffusion flux obeys equation (26). Not surprisingly, film theory works well when the actual physical situation agrees with the above model, but can be inaccurate under other conditions. We will say more about film theory later in the course when we'll take a look at mass transfer coefficients.

Importantly, steady-state 1-dimensional diffusion through a stagnant film represents an important limiting scenario. Imagine a film, permeable to species $A$, sandwiched between two very large reservoirs. The left reservoir contains $A$ solute while the right reservoir is pure solvent, Fig. 3. Diffusion of $A$ from the left to the right reservoir will ensue in order to bring the two reservoirs into equilibrium. Forced and free convection in the film are assumed to be absent. Let's imagine that the diffusion starts at $t = 0$, at which time $A$ molecules first begin to enter the film from the left reservoir. Then, at short times, the concentration of $A$ in the film will rise (starting from the left edge of the film) as $A$ molecules begin penetrating the film on their way from the left to the right reservoir. Because the concentration of $A$ in the film is changing with time, this early diffusion is *not* a steady state process. However, after sufficient time has elapsed, steady-state will be established in which the concentration profile of $A$ across the film is no longer changing significantly. From this time forward, the diffusion process of Fig. 3 corresponds to the above steady state solution for one-dimensional diffusion (Note: adjustments for different boundary conditions, for instance using partitioning coefficients rather than vapor pressures to express $y_{AS}$ and/or $y_{A0}$, may be needed based on specifics of the problem).

![Diagram of diffusion](image.png)

**Fig. 3**

The next example will consider unsteady, one-dimensional diffusion into a semi-infinite medium. Where one-dimensional *steady state* diffusion, studied above, represents the long time limit for the diffusion process of Fig. 3, one-dimensional *unsteady* diffusion into a semi-infinite medium represents the short time limit. Even though the film in Fig. 3 is not semi-infinite, at short times species $A$ has not yet reached the right edge of the film and so the presence of a boundary at $z = L$ does not affect its diffusion – hence, at sufficiently short times, the film
behaves identically to a semi-infinite medium. Collectively, the two examples of (i) one-dimensional steady state diffusion (discussed above) and (ii) one-dimensional unsteady diffusion (discussed below), bracket many observed phenomena since they represent, respectively, the long time and short time limiting behavior of 1-dimensional diffusion processes.

3. Unsteady, One-Dimensional Diffusion Into A Semi-Infinite Medium (Dilute Case).

Fig. 4 depicts the problem at hand. At time \( t = 0 \), two semi-infinite media are brought together such that their shared interface is at \( z = 0 \). The left medium (medium I) is well-stirred, and has a uniform concentration \( c_{\text{AI}} \) of solute A in a solvent. The right medium (medium II, consisting of material B) has an initial concentration of A that is uniform and equal to \( c_{\text{A0}} \). As soon as the two media are contacted, local equilibrium establishes a concentration \( c_{\text{AS}} \) of A just inside medium II equal to

\[
  c_{\text{AS}} = c_{\text{AII}}(z = 0) = Hc_{\text{AI}}
\]

where \( H \) is the partitioning coefficient. Also, it will be assumed that

\[
  c_{\text{AS}} > c_{\text{A0}}
\]

Inequality (39) implies that A diffuses from medium I to medium II. It will moreover be assumed that medium I is very large, and is not significantly depleted of A by the diffusion, and that medium I is well-stirred, so that concentration of A remains uniform and equal to the initial concentration \( c_{\text{AI}} \) everywhere in medium I. This implies that the boundary concentration in medium II, \( c_{\text{AS}} \), also does not change with time.

Also given:
(i) no chemical reactions in medium II
(ii) no forced or free convection in medium II
(iii) diffusion of A into medium II occurs under dilute conditions, so that diffusion-engendered convection is negligible
(iv) a constant diffusion coefficient \( D_{\text{AB}} \)
Determine the concentration of $A$ in medium II as a function of time $t$ and position $z$.

**Solution.** The species’ conservation equation for species $A$ in medium II is

$$\frac{\partial c_A}{\partial t} = -\nabla \cdot N_A + R_A \tag{40}$$

Since there are no reactions in medium II (given condition (i)),

$$R_A = 0 \tag{41}$$

Since the diffusion occurs under dilute conditions, diffusion-engendered convection is absent (condition (iii)). Furthermore, forced and free convection are absent (condition (ii)). Under these simplifications the total molar flux $N_A$ equals the diffusive flux $J_A$,

$$N_A = J_A \tag{42}$$

Furthermore, according to Fick's Law,

$$J_A = -D_{AB} \nabla c_A \tag{43}$$

From the one-dimensional geometry of the problem, we expect that $c_A$ will only vary with $z$ (i.e. $c_A$ does not depend on $x$ or $y$). Then

$$J_A = -D_{AB} (\partial c_A/\partial z) \delta z \tag{44}$$

Inserting (44) and (41) into the PDE equation (40) leads to

$$\frac{\partial c_A}{\partial t} = -\nabla \cdot \{ -D_{AB} (\partial c_A/\partial z) \delta z \} = -\left( \frac{\partial}{\partial x} \delta_x + \frac{\partial}{\partial y} \delta_y + \frac{\partial}{\partial z} \delta_z \right) \cdot \{ -D_{AB} (\partial c_A/\partial z) \delta z \} \tag{45}$$

or

$$\frac{\partial c_A}{\partial t} = D_{AB} \frac{\partial^2 c_A}{\partial z^2} \tag{46}$$

In deriving equation (46), it was assumed that $D_{AB}$ is constant (given condition (iv)). To complete the problem, (46) must be supplemented by an initial condition on $t$ and two boundary conditions on $z$, in medium II where the concentration is to be derived. These conditions come directly from the problem statement,

**Initial condition:** \[ c_A(t = 0, z) = c_{A0} \quad z > 0 \tag{47} \]

**Boundary conditions:**

- $c_A(t, z = 0) = c_{AS} = Hc_{AI} \quad t > 0 \tag{48}$
- $c_A(t, z = \infty) = c_{A0} \quad t > 0 \tag{49}$
Equation (49) states that, infinitely far from the interface with medium I, the concentration in medium II remains at the initial value of $c_{A0}$. This condition reflects the physical expectation that species $A$ will not penetrate infinitely far into medium II no matter how long a time has elapsed.

Equations (46) to (49) completely specify the problem. The PDE (46) can be solved using the method of Laplace transforms. A Laplace transform approach is often successful for initial value problems. An initial value problem is one in which an independent variable ($t$ in equation (46)) on which the unknown function ($c_A$ in equation (46)) depends varies from 0 to $\infty$, and the solution needs to predict how the function of interest evolves as this variable rises to infinity. In what follows, this independent variable will be referred to as the "initial value" variable.

We recall that the Laplace transform $L(f)$ of a function $f$ is defined by

$$L(f) = \int_0^\infty e^{-st} f \, dt$$

(50)

Since $s$ will stay after the integral is evaluated, the transform $L(f)$ is a function of $s$, and is defined for all $s$ for which the integral in (50) converges. It will be assumed that the function $f$ is a continuous function of the initial value variable $t$, where $t$ can assume values from 0 to $\infty$. $f$ can also be a function of other independent variables, such as position variables $x$, $y$, and $z$.

Integration by parts can be used to show that the Laplace transform of a first order derivative of $f$ with respect to the initial value variable $t$ is given by

$$L\left(\frac{\partial f}{\partial t}\right) = sL(f) - f(t = 0)$$

(51)

When the function $f$ depends on a second variable $q$ in addition to $t$, then

$$\frac{dL(f)}{dq} = L(\frac{\partial f}{\partial q})$$

(52)

Equation (52) states that the derivative of the Laplace transform of $f$ with respect to $q$ equals the Laplace transform of the derivative of $f$ with respect to $q$. In other words, the order of differentiation with respect to $q$ and performance of the Laplace transform is interchangeable. Differentiation of (52) with respect to $q$ leads to (again making use of the interchangeability of order of performance of the differentiation and the transform)

$$\frac{d^2L(f)}{dq^2} = L(\frac{\partial^2 f}{\partial q^2})$$

(53)

This brief review of Laplace transforms sets the stage for solving the posed problem. First, we take the Laplace transform of equation (46) with respect to $t$,

$$L\left(\frac{\partial c_A}{\partial t}\right) = D_{AB} L\left(\frac{\partial^2 c_A}{\partial z^2}\right)$$

(54)

According to (51), the left hand side of (54) becomes
\[
L \left( \frac{\partial c_A}{\partial t} \right) = s \ L(c_A) - c_A(t = 0) = s \ L(c_A) - c_{A0}
\]  
(55)

It is noted that the initial condition, equation (47), was already incorporated into (55). This condition will therefore not be needed again. Making use of equation (53), the right hand side of equation (54) becomes

\[
D_{AB} \ L \left( \frac{\partial^2 c_A}{\partial z^2} \right) = D_{AB} \left( \frac{d^2 L(c_A)}{dz^2} \right)
\]  
(56)

Using equations (55) and (56), the Laplace transform of the PDE equation (46) is

\[
s \ L(c_A) - c_{A0} = D_{AB} \left( \frac{d^2 L(c_A)}{dz^2} \right)
\]

or

\[
\left( \frac{d^2 L(c_A)}{dz^2} \right) - s \ L(c_A)/D_{AB} + c_{A0}/D_{AB} = 0
\]  
(57)

Equation (57) is an ODE for the function \( L(c_A) \). Taking the Laplace transform of the PDE equation (46) has removed the derivative with respect to time, thus converting the PDE into an ODE. The boundary conditions on \( c_A \), equations (48) and (49), also need to be transformed to boundary conditions on \( L(c_A) \),

\[
\begin{align*}
L(c_A(z = 0)) &= c_{AS}/s = Hc_{AI}/s \\
L(c_A(z = \infty)) &= c_{A0}/s
\end{align*}
\]  
(58)

Equations (58) and (59) follow from the Laplace transform of a constant \( C \),

\[
L(C) = \int_0^\infty e^{-st} \ C \ dt = C/s
\]  
(60)

The ODE equation (57), supplemented by boundary conditions (58) and (59), can now be solved. (57) is a second order, linear, inhomogeneous ODE (inhomogeneous because of the \( c_{A0} \) term). Inhomogeneous ODE's are usually solved by (i) obtaining a solution to the homogeneous version of the ODE (i.e. with \( c_{A0} \) set to 0), (ii) obtaining a so-called **particular solution** that satisfies the full inhomogeneous ODE, and (iii) adding the homogeneous and particular solutions together to get the complete solution. The boundary conditions are enforced on the complete solution. This procedure is followed below.
The homogeneous equation associated with (57) is
\[
\left( \frac{d^2 L_H(c_A)}{dz^2} \right) - s \frac{L_H(c_A)}{D_{AB}} = 0
\]  
(61)

The subscript "H" on \( L_H(c_A) \) signifies it is the solution to the homogeneous equation. The equation is second order, linear in \( L_H(c_A) \), and possesses constant coefficients. This type of equation always has an exponential solution of the form \( \exp[-rz] \). The handout on heat conduction reviewed how to solve such equations, and only an abbreviated procedure is given here. The characteristic equation to (61) is
\[
r^2 - \frac{s}{D_{AB}} = 0
\]  
(62)

so that
\[
r = \pm \sqrt{\frac{s}{D_{AB}}}
\]

Therefore, the general solution to the homogeneous equation (61) is
\[
L_H(c_A) = C_1 \exp[z \left( \frac{s}{D_{AB}} \right)^{1/2}] + C_2 \exp[-z \left( \frac{s}{D_{AB}} \right)^{1/2}]
\]  
(63)

Next, we need to find one particular solution, \( L_P(c_A) \), that satisfies the full inhomogeneous ODE (57). This is easy in the present case. Specifically, by inspection we see that if we assume \( L_P(c_A) \) is simply a constant \( C_P \), then (57) becomes
\[
0 - s \frac{C_P}{D_{AB}} + \frac{c_A0}{D_{AB}} = 0
\]  
(64)

Thus, setting
\[
C_P = \frac{c_A0}{s} \quad ( = L_P(c_A))
\]  
(65)

will satisfy equation (64) and therefore produce a particular solution to the inhomogeneous equation (57). Addition of the homogeneous (equation (63)) and particular (equation (65)) solutions produces the full solution for \( L(c_A) \),
\[
L(c_A) = C_1 \exp[z \left( \frac{s}{D_{AB}} \right)^{1/2}] + C_2 \exp[-z \left( \frac{s}{D_{AB}} \right)^{1/2}] + \frac{c_A0}{s}
\]  
(66)

Equation (66) is subject to two boundary conditions. First, boundary condition (59) requires
\[
L(c_A(z = \infty)) = \frac{c_A0}{s}
\]  
(59)

By inspection of (66), we see that to satisfy (59) we must set \( C_1 = 0 \); otherwise, the first right term in (66) diverges as \( z \to \infty \). With the first right term eliminated, equation (66) becomes
\[
L(c_A) = C_2 \exp[-z \left( \frac{s}{D_{AB}} \right)^{1/2}] + \frac{c_A0}{s}
\]  
(67)
what now satisfies the boundary condition (59). In addition, equation (67) must also satisfy boundary condition (58),

\[ L(c_A(z = 0)) = \frac{c_{AS}}{s} \]  

(58)

Applying (58) to (67) leads to

\[ \frac{c_{AS}}{s} = C_2 + \frac{c_{A0}}{s} \]  

(68)

Therefore,

\[ C_2 = \frac{(c_{AS} - c_{A0})}{s} \]  

(69)

and the complete solution for the Laplace transform of \( c_A \) is

\[ L(c_A) = (c_{AS} - c_{A0}) \left( \frac{1}{s} \right) \exp\left[ -z \left( \frac{s}{D_{AB}} \right)^{1/2} \right] + \frac{c_{A0}}{s} \]  

(70)

Equation (70) is the Laplace transform of the desired concentration profile \( c_A \). It satisfies both boundary conditions as well as the initial condition incorporated previously. All that remains to be done is to take the inverse Laplace transform of equation (70) in order to obtain \( c_A \). In other words, we have to figure out what function for \( c_A \) would produce the Laplace transform \( L(c_A) \) as given in equation (70). This is easily accomplished through the use of tables of functions and their Laplace transforms (most ODE textbooks have such tables). From such tables we could learn that

\[ L\left( \text{erfc}\left( \frac{a}{2\sqrt{t}} \right) \right) = \left( \frac{1}{s} \right) \exp\left[ -a \left( \frac{s}{D_{AB}} \right)^{1/2} \right] \]  

(71)

where \( \text{erfc}(x) \) is the **complementary error function**, defined by

\[ \text{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-w^2} dw \]  

(72)

By inspection of (70) and (71), if we set \( a = z / (D_{AB})^{1/2} \) in (71) then the right hand side in (71) is the same as the first right term in (70) except for the constant multiplying factor \( (c_{AS} - c_{A0}) \). In other words, the Laplace transform of the function

\[ (c_{AS} - c_{A0}) \text{erfc}\left( \frac{z}{2\sqrt{D_{AB}t}} \right) \]

is equal to the first right term in (70). The second right term in equation (70), \( c_{A0}/s \), is a Laplace transform of the constant \( c_{A0} \) (see equation (60)). The sum of the two terms,
The diffusive flux $J_{Az}$ into medium II across the boundary at $z = 0$ can be calculated by applying Fick's law to the concentration profile equation (73),

$$J_{Az} \big|_{z=0} = -D_{AB} \left( \frac{dc_A}{dz} \right)_{z=0} = -D_{AB} \frac{d}{dz} \left( (c_{AS} - c_{A0}) (1 - \frac{z}{2} \sqrt{D_{AB} t}) \right) _{z=0}$$

$$= D_{AB} (c_{AS} - c_{A0}) \left[ \frac{2}{\sqrt{\pi}} \right] \left[ e^{-z^2/4D_{AB}t} \frac{1}{2\sqrt{D_{AB} t}} \right] _{z=0}$$
Because bulk convection was assumed to be negligible, the diffusive molar flux is taken equal to the total molar flux, \( J_{Az \mid z=0} = N_{Az \mid z=0} \). Equation (74) predicts that the rate of mass transfer into medium II decreases with the inverse square root of time.

In conclusion, it is useful to re-emphasize that unsteady, one-dimensional diffusion into a semi-infinite medium is an excellent approximation to early stage diffusion into slabs or films whose width is finite. As long as the concentration profile \( c_A \) (equation (73)) has not penetrated sufficiently to span across the width of such a slab the above formulas for flux and \( c_A \) should be good approximations. For example, if species \( A \) is penetrating into a slab of width \( L \), as long as \( c_A(z = L) \) remains below a chosen value (e.g. \( c_A(z = L) < 0.01c_{AS} \)) application of the above formulas could be deemed acceptable.