1

Introduction to Simultaneous Mass Transfer and Chemical Reactions in Engineering Science

In many biochemical, biomedical, and chemical processes, in both the chemical industry and in physiological systems, including environmental sciences, mass transfer, accompanied by reversible, complex biochemical, or in chemical reactions in gas–liquid systems, is frequently found. From the viewpoint of biochemical and/or chemical design purposes, it is very important that the absorption rates of the transferred reactants may be estimated accurately.

Moreover, the mass transfer phenomena can also affect substantially important process variables like selectivity and yield. Considerable research effort has been expended in describing these processes and in the development of mathematical models that may be used for the computation of the mass transfer rates and other parameters.

For example, the description of the absorption of a gas followed by a single first-order reversible reaction is simple and straightforward. For all mass transfer models, e.g. film, surface renewal, and penetration, this process may be analytically solved. For other processes, however, only for a limited number of special cases analytical solutions are possible, and therefore numerical techniques must be used for the description of these phenomena. Besides numerically solved absorption models, the mass transfer rates often may be calculated, with sufficient accuracy by simplifying the actual process by means of approximations and/or linearizations. In this book, an overview will be given of the absorption models that are available for the calculation of the mass transfer rates in gas–liquid systems with (complex) reversible reactions. Both numerically solved and approximated models will be treated and conclusions on the applicability and restrictions will be presented.

1.1 Gas–Liquid Reactions

It is well known that many biochemical and chemical processes involve mass transfer of one or more species from the gas phase into the liquid phase. In the liquid phase, the species from the gas phase are converted by one or more (possibly irreversible) biochemical or chemical reactions with certain species present in the liquid phase.

Typical of such examples are provided in Sections 1.1.1.1 and 1.1.1.2.

Simultaneous Mass Transfer and Chemical Reactions in Engineering Science, First Edition. Bertram K. C. Chan.

1.1.1 Simultaneous Biomolecular Reactions and Mass Transfer

1.1.1.1 The Biomedical Environment

In epidemiologic investigations, occurrences of simultaneous biomolecular reactions and mass transfer are common in many biomedical environments. Some typical examples are:

(1) **Intestinal Drug Absorption Involving Bio-transporters and Metabolic Reactions with Enzymes** [1]: The absorption of drugs via the oral route is a subject of on-going and serious investigations in the pharmaceutical industry since good bio-availability implies that the drug is able to reach the systemic circulation via the oral path. Oral absorption depends on both the *drug properties* and the physiology of the gastrointestinal tract, or *patient properties*, including drug dissolution, drug interaction with the aqueous environment and membrane, permeation across membrane, and irreversible removal by organs such as the liver, intestines, and the lung.

(2) **Oxygen Transport via Metal Complexes** [1]: On average, an adult at rest consumes 250 ml of pure oxygen per minute to provide energy for all the tissues and organs of the body, even when the body is at rest. During strenuous activities, such as exercising, the oxygen needs increase dramatically. The oxygen is transported in the blood from the lungs to the tissues where it is consumed. However, only about 1.5% of the oxygen transported in the blood is dissolved directly in the blood plasma. Transporting the large amount of oxygen required by the body, and allowing it to leave the blood when it reaches the tissues that demand the most oxygen, require a more sophisticated mechanism than simply dissolving the gas in the blood. To meet this challenge, the body is equipped with a finely tuned transport system that centers on the metal complex ***heme***. The metal ions bind and then release ligands in some processes, and to oxidize and reduce in other processes, making them ideal for use in biological systems. The most common metal used in the body is iron, and it plays a central role in almost all living cells. For example, iron complexes are used in the transport of oxygen in the blood and tissues. Metal–ion complexes consist of a metal ion that is bonded via "coordinate-covalent bonds" to a small number of anions or neutral molecules called ligands. For example, the ammonia (NH_3) ligand is a mono-dentate ligand; i.e. each mono-dentate ligand in a metal–ion complex possesses a single electron-pair-donor atom and occupies only one site in the coordination sphere of a metal ion. Some ligands have two or more electron-pair-donor atoms that can simultaneously coordinate to a metal ion and occupy two or more coordination sites; these ligands are called polydentate ligands. They are also known as chelating (Greek word for "claw") agents because they appear to grasp the metal ion between two or more electron-pair-donor atoms. The coordination number of a metal refers to the total number of occupied coordination sites around the central metal ion (i.e. the total number of metal–ligand bonds in the complex). This process is another important example of biomolecular reaction and transport.

(3) **Carotenoid Transport in the Lipid Transporters SR-BI, NPC1L1, and ABCA1**: The intestinal absorption of carotenoids in vivo involves several crucial steps:
    (1) release from the food matrix in the lumen
    (2) solubilization into mixed micelles
    (3) uptake by intestinal mucosal cells
    (4) incorporation into chylomicrons
    (5) secretion into the lymph.

    Research has shown that:
    (A) EZ is an inhibitor of the intestinal absorption of carotenoids, an effect that decreased with increasing polarity of the carotenoid molecule
    (B) SR-BI is involved in intestinal carotenoid transport
    (C) EZ acts not only by interacting physically with cholesterol transporters as previously suggested but also by downregulating the gene expression of three proteins involved in cholesterol transport in the enterocyte, the transporters SR-BI, NPC1L1, and ABCA1.

    The intestinal transport of carotenoid is thus a facilitated process resembling that of cholesterol; therefore, carotenoid transport in intestinal cells may also involve more than one transporter.

    Hence, the study of biomolecular reaction and transport is an area of importance in biomedical processes and their occurrences in epidemiologic investigations.

    In this section, one applies the facilities available in the R environment to solve problems arisen from these processes. This study is being approached from two directions:
    - Using the R environment as a ***support*** to numerical analytical schemes that may be developed to solve this class of problems.
    - Applying the R functions in the CRAN package ReacTran [2].

1.1.1.2 The Industrial Chemistry and Chemical Engineering Environment

Typical examples of industrial chemical and chemical engineering processes in which this phenomenon occurs include chlorination, gas purification, hydrogenation, and oxidation processes. To undertake the process and equipment design of new reactors and the optimization of existing reactors, applicable theoretical models for reactors are helpful and most likely needed. In general, models of liquid–gas contactors consist of two main parts: the ***micro model*** and the ***macro model***:

- the **micro** model describes the interphase mass transfer between the gas phase and the liquid phase,
- the **macro** model describes the mixing behavior in both phases.

Both parts of the overall model may be solved sequentially, but solving micro and macro models simultaneously is preferred because of optimization of computational time.

Gas–liquid mass transfer modeling has been well studied. The Whitman stagnant film model was first described in 1923 by W.G. Whitman, and it was concluded that some phenomena of gas–liquid mass transfer may be regarded as nearly incompletely explained. Moreover, the Higbie penetration model has been used as a basis for the development of some new reactor models. The influence of the bulk liquid on the mass transfer process has been studied in some detail. More attention has been paid to the dynamical behavior and stability of gas–liquid reactors and the influence of mass transfer limitations on the dynamics. Also, some important differences between the results of the Higbie penetration model and the Whitman stagnant film model are found.

Analytical solution of micro models for mass transfer (accompanied by chemical reactions) is restricted to asymptotic cases in which many simplifying assumptions had to be made (e.g. reaction kinetics are simple and the rate of the reaction is either very fast or very slow compared to the mass transfer). For all other situations, numerical–computational techniques are required for solving the coupled mass balances of the micro model.

In general, it seems that mostly numerical solution techniques have been applied. Wherever possible, analytical solutions of asymptotic cases have been used to check the validity of the numerical solution method.

For example, by modifying one of the boundary conditions of the Higbie penetration model, it had been found that the mass transfer may be affected by the presence of the bulk liquid. For example, in a packed column, the liquid flows down the column as a thin layer over the packings. It has been examined whether or not the penetration model may be applied for these configurations. Both physical absorption and absorption accompanied by first- and second-order chemical reactions have been investigated.

From model calculations, it is concluded that the original penetration theory, by assuming the presence of a well-mixed liquid bulk, may be applied also to systems where no liquid bulk is present, provided that the liquid layer is sufficiently thick!

- For packed columns this means, in terms of the Sherwood number, $N_{Sh} = 4$, for both physical absorption and absorption accompanied by a first-order reaction.
- In case of a second-order 1,1-reaction, a second criterion: $N_{Sh} \geq 4\sqrt{(D_\mathrm{b}/D_\mathrm{a})}$ has to be fulfilled.
- For very thin liquid layers ($N_{Sh} < 4$, or $N_{Sh} < 4\sqrt{(D_\mathrm{b}/D_\mathrm{a})}$), the original penetration model may give erroneous results, depending on the exact physical and chemical parameters, and a modified model is required.

Analytical solution of models for gas–liquid reactors is restricted to a few asymptotic cases, while most numerical models make use of the physically less realistic stagnant film model – this is relatively simplistic and easy to apply using the "**hinterland model**." *The hinterland model assumes the reaction phase to consist of ONLY a stagnant film and a well-mixed bulk. Inflow and outflow of species to and from the reactor proceeds via the non-reaction phase or via the bulk of the reaction phase, but never via the stagnant film. ("Hinterland" is a German word meaning "the land behind" [a port, a city, …] in geographic usages!)*

By modifying one of the boundary conditions of the Higbie penetration model, it illustrated how the mass transfer may be affected by the presence of the liquid bulk. Thus, for example, in a packed column, the liquid flows as a thin layer over the structured or dumped packing. It has been examined whether or not the penetration model can be applied for these situations. Both physical absorption and absorption accompanied by first- and second-order chemical reactions have been investigated.

From model calculations, it is concluded that the original penetration theory, which assumes the presence of a well-mixed liquid bulk, may be applied also to systems where no liquid bulk is present, provided that the liquid layer has sufficient thickness.

For packed columns, this means, in terms of Sherwood number, $Sh > 4$ for both physical absorption and absorption accompanied by a first-order reaction. In case of a second-order 1,1-reaction a second criterion $Sh \geq 4\sqrt{(D_b/D_a)}$ has to be fulfilled. For very thin liquid layers, $Sh < 4$ or $Sh < \sqrt{(D_b/D_a)}$, the original penetration model may give erroneous results, depending on the exact physical and chemical parameters, and the modified model is required.

Most numerical models of gas–liquid reactors make use of the physically less realistic stagnant film model because implementation of the stagnant film model is relatively easy using the hinterland concept. The combination of stagnant film model and Hinterland concept may successfully predict many phenomena of gas–liquid reactors.

The Higbie penetration model is however preferred as a micro model because it is physically more realistic. Direct implementation of the hinterland concept is not possible with the Higbie penetration model. Nevertheless, numerical techniques have been applied to develop a new model that implements the Higbie penetration model for the phenomenon mass transfer accompanied by chemical reaction in well-mixed two-phase reactors: assuming the stagnant film.

A model was developed that simulates the dynamic behavior of gas–liquid tank reactors by simultaneously solving the Higbie penetration model for the phenomenon of mass transfer accompanied by chemical reaction and the dynamic gas and liquid phase component balances. The model makes it possible to implement an alternative for the well-known hinterland concept, which is usually used together with the stagnant film model. In contrast to many other numerical and analytical models, the present model can be used for a wide range of conditions, the entire range of Hatta numbers, (semi-)batch reactors, multiple complex reactions, and equilibrium reactions, components with different diffusion coefficients, and also for systems with more than one gas phase component. By comparing the model results with analytical asymptotic solutions, it was concluded that the model predicts the dynamic behavior of the reactor satisfactorily. It had been shown that under some circumstances, substantial differences exist between the exact numerical and existing approximate results. It is also known that for some special cases, differences can exist between the results obtained using the stagnant film model with hinterland concept and the implementation of the Higbie penetration model.

Analytical solution of models for gas–liquid reactors is restricted to a few asymptotic cases, while most numerical models make use of the physically less realistic stagnant film model.

1.1.2 Conclusions

1. The penetration model is preferred for the phenomenon mass transfer accompanied by chemical reaction in well-mixed two-phase reactors.
2. By comparing the model results with analytical asymptotic solutions, it is concluded that the model predicts the reactor satisfactorily. It is shown that for many asymptotic cases, the results of this new model coincide with the results of the stagnant film model with hinterland concept.
3. For some special conditions, differences may exist between the results obtained using the stagnant film model with hinterland concept and the implementation of the Higbie penetration model.
4. An important result is that for 1,1-reactions, the saturation of the liquid phase with gas phase species does not approach zero with increasing reaction rate (increasing Hatta number), contrary to what is predicted by the film model with Hinterland concept. Another important deviation may be found at the specific conditions of a so-called instantaneous reaction in combination with the absence of chemical enhancement of mass transfer.
5. Application of the penetration model does not provide any numerical difficulties, while application of the stagnant film model would lead to a discontinuity in the concentration gradient.
6. Another disadvantage of the hinterland concept is that it can strictly only be applied to isothermal systems, whereas in the systems investigated in this thesis the reaction enthalpy is an important parameter that may significantly influence the phenomena of gas–liquid mass transfer.

A rigorous model may be developed that simulates the dynamic behavior of stirred nonisothermal gas–liquid reactors by simultaneously solving the Higbie penetration model for the phenomenon mass transfer accompanied by chemical reaction and the dynamic gas and liquid phase component and heat balances. This is achieved by coupling the ordinary differential equations of the macro model mass and heat balances to the partial differential equations of the penetration model. This model is not yet published!

Using the newly developed rigorous reactor model, it is shown that dynamic instability (limit cycles) can occur in gas–liquid reactors. The influence of mass transfer limitations on these limit cycles has been studied, and it has been found that mass transfer limitations make the process more stable.

1.1.3 Summary

Although the rigorous model is believed to be a very accurate model, it has the disadvantage that owing to the complex numerical methods applied it is a rather time-consuming model. On behalf of a more efficient prediction of the possible occurrence of limit cycles, the reactor model was simplified. The simplified model is suited for the prediction of limit cycles using a stability analysis. A stability analysis is a very efficient method to predict the dynamic behavior and stability of a system of ordinary differential equations by linearization of the governing nonlinear ODEs in the neighborhood of the steady state and analyzing the Eigenvalues. This method is very powerful for attaining design rules for stable operation of stirred gas–liquid reactors. The influence of mass transfer limitations on the limit cycles is predicted very well using the simplified model, though small discrepancies are found with the more accurate rigorous model.

The developed reactor models have been used to model the dynamics of a new, to-be-developed, industrial hydro-formylation reactor. At a certain design of the reactor, the model predicts serious and undesired limit cycles. These conditions have to be avoided by an appropriate reactor design. Hydro-formylation reactions are often characterized by a negative reaction order in carbon monoxide. Model calculations showed that this may lead to interesting phenomena: at certain process conditions, an improvement of the mass transfer (higher $k_L a$, for example, owing to improved mixing) may give rise to a less stable reactor, without increasing the conversion. This unusual phenomenon is explained by the negative reaction order of carbon monoxide. Apparently, the increasing hydrogen and carbon monoxide concentrations cancel each other out and the overall reaction rate remains unchanged. The increasing hydrogen and carbon monoxide concentrations do however make the process more sensitive for the occurrence of limit cycles.

Finally, a start has been made with studying the influence of macro-mixing on the dynamical behavior of gas–liquid reactors. For this purpose, a cascade of two reactors in series is compared to a single reactor. Initial results indicate that a cascade of reactors in series provides a dynamically more stable design. The total required cooling surface to prevent the occurrence of temperature–concentration limit cycles decreases significantly with increasing number of reactors in series. The first reactor in the cascade is the one with the highest risk of dynamic instability.

1.2 The Modeling of Gas–Liquid Reactions

This process has evolved through a number of theoretical processes, including:

1.2.1 Film Theory of Mass Transfer

In typical industrial absorption processes, one should consider the absorption of gases into liquids which are agitated such that the dissolved gas is transported from the surface to the interior by convective motions. The agitation may occur in various ways, including:

(i) The gas, or vapor, may be blown through the liquid as a stream of bubbles – as, for example, on a perforated plate or in a sparged vessel.

(ii) The liquid may be running in a layer over an inclines or vertical surface, and the flow may be turbulent (as, for example, in a wetted-wall cylindrical column operating at a sufficiently high Reynolds number), or ripples may develop and enhance the absorption rate by convective motion. Discontinuities on the surface may cause periodic mixing of the liquid in the course of its flow, or strings of discs or of spheres.

(iii) The liquid may be advantageously agitated by a mechanical stirrer, which may also entrain bubbles of gases into the liquid.

(iv) The liquid may be sprayed through the gas as jets or drops. First consider a steady-state situation in which the composition of the liquid and gas, averaged over a specified region and also with respect to any temporal fluctuations, are statistically constant. For example, one may consider an agitated vessel through which liquid and gas flow steadily, both being so thoroughly mixed that their time-average compositions are the same at all points; or one may consider a short vertical section of a packed column (or sphere or disc or wetted-wall column) operating at steady state, such that the average compositions of the liquid and gas in the element remain *constant* with time.

Clearly, the situation is a complicated one: the concentrations of the various species are not uniform or constant when measured over short length and time scales. Diffusion, convection, *and* reaction proceed simultaneously. The nature of the convective movements of liquid and gas is difficult to define: any attempt to describe them completely would encounter considerable complications. Thus, to obtain useful predictions about the behavior of such systems for practical purposes, it is necessary to use simplified models which simulate the situation sufficiently well, without introducing a large number of unknown parameters. This approach may take a number of simplifying steps, as follows:

(A) Physical Absorption [2]

Consider first physical absorption, in which the gas dissolves in the liquid *without* any reaction; it is found experimentally that the rate of absorption of the gas is given by

$$\underline{R}_{\mathrm{a}} = k_{\mathrm{L}}a(A^{*} - A^{0}) \tag{1.1}$$

in which A^* is the concentration of dissolved gas at the interface between gas and liquid, assuming this partial pressure to be uniform throughout the element of space under discussion. The area of interface between the gas and liquid, per unit volume of the system, is a and k_{L} is the “physical mass-transfer coefficient.” $\underline{R}$ is the rate of transfer which may vary from point to point and from time to time. $\underline{R}$ is the average rate of transfer of gas per unit area; the actual rate of transfer may vary from point to point, and from time to time. A^0 is the average concentration of dissolved gas in the bulk of the liquid.

It is usually not possible to determine k_{L} and a separately, by measurements of physical absorption. For example, in a packed column, the fraction of the surface of packings which is effectively wetted is unknown, and in a system containing bubbles, the interfacial area is ***not*** generally known! Thus, the quantity directly measurable by physical absorption measurements is the combined quantity $k_\mathrm{L}a$.

Hence, the validity of Eq. (1.1) has been established in numerous experimental studies, and an expression of this form would be predicted from first principles, provided that certain conditions are met. The chief of these are that the temperature and diffusivity at the surface (where the concentration is A^*) should be very different from those in the bulk of the liquid; and that no chemical reaction occurs, so that all molecules of dissolved gas are in the same condition. It is sometimes difficult to decide whether a solute reacts chemically with a liquid or merely interacts with it physically. From the present purpose, “physical” solution means that it molecules are indistinguishable.

1.2.2 Surface Renewal Theory of Mass Transfer

Models evolved under this theory take as their basis the replacement at time intervals of liquid at the surface by liquid from the interior which has the local mean bulk composition. While the liquid element is at the surface and is exposed to the gas, it absorbs gas as though it were infinitely deep and quiescent: the rate of absorption, R, is then a function of the exposure time of the liquid element and will be described by a suitable expression such as those to be described by the reaction kinetics of the system. In general, the rate of absorption is fast or infinite initially, decreasing with time. The replacement of liquid at the surface by fresh liquid of the bulk composition may be due to the turbulent motion of the body of the liquid. Moreover, when liquid runs over the surface of a packing, it may be in a state of undisturbed laminar flow at the top of each piece of packing, except at the discontinuities between pieces of packing, where it may mix thoroughly: at the top of each piece of packing, a fresh surface would then be developed and moved discontinuity, when it would then be replaced again by fresh liquid.

With this scenario, the surface-renewal models propose that the surface of an agitated liquid, or a liquid flowing over a packing, is a collection of elements which have been exposed to the gas for different durations of time, and which may well be, in general, absorbing at different specific rates. Thus, different versions of the model will lead to different specific rates. Moreover, different versions of the model will lead to different distributions of surface ages about the mean value. The form of the surface-renewal model first proposed by Higbie, in 1935, assumed that every element of surface is exposed to the gas for the ***same*** duration of time, θ, before being replaced by liquid of the bulk composition. During this time, the element of liquid absorbs the same amount Q of gas per unit area as though it were infinitely deep and stagnant. The average rate of absorption is therefore Q/θ, and this is also the rate of absorption $\underline{R}$ per unit area averaged over the interface in a representative region of a steady-state absorption system in which the bulk composition is statistically uniform – e.g. in a small, but representative, volume element of a packed column.

The exposure-time θ may be determined by the hydrodynamic properties of the system, and is the only parameter required to account for their effect on the transfer coefficient k_L. The relation between θ and k_L is derived herebelow – in physical absorption.

Under such circumstances, the variation in time and space of the concentration a of dissolved gas in the liquid in the absence of reaction is governed by the diffusion

$$D_A\, \partial^2 a/\partial x^2 = \partial a/\partial t \tag{1.2}$$

And the rate of transfer of dissolved gas initial concentration passage of gas across the interface, then the concentration of the surface might vary with time. For the present, it is assumed that the diffusion of dissolved gas into the latter. This assumption generally holds when the solubility of the gas is not very great, so that A^* represents a mole fraction much less than unity.

It would not be true, for example, if ammonia at atmospheric pressure were diffusing into pure water (in which there will be a substantial temperature rise). Under these conditions, the variation in time and space of the concentration, a, of dissolved gas in the liquid in the absence of reaction as governed by the diffusion from bubbles or absorption by wetted-wall columns, the mass transfer surface is formed instantaneously and transient diffusion of the material takes place. Assuming that a bubble is rising in a pool of liquid (where the liquid elements are swept on its surface) and remains in contact with it during their motion and finally detached at the bottom.

The basic assumptions of the penetration theory are:

- Unsteady-state mass transfer occurring to a liquid element as long as it is in contact with the gas bubbles
- Equilibrium existing at gas–liquid interface
- Each liquid element staying in contact with the gas for same period of time. (The liquid elements are moving at the same rate, and there is not a velocity gradient within the liquid.)

Under these assumptions, the convective terms in the diffusion may be neglected and the unsteady-state mass transfer of gas (penetration) into the liquid element may be written from Fick's second law for unsteady-state diffusion as (Figure 1.1)

$$\partial c/\partial t = D_{AB}(\partial^2 c/\partial z^2) \tag{1.3}$$

and the boundary conditions are

$$t = 0, z > 0: \quad c = c_{Ab}$$

and

$$t > 0, z = 0: \quad c = c_{Ai}$$

where

c_{Ab} = The concentration of solute A at an infinite distance from the surface (viz. the bulk concentration)

c_{Ai} = The interfacial concentration of solute A at the surface

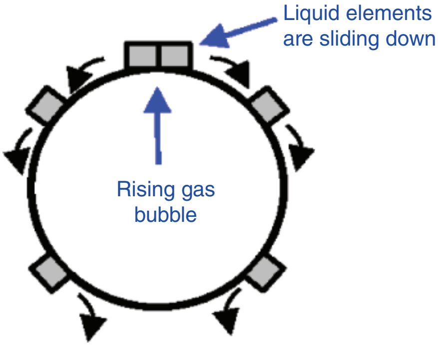

Figure 1.1 Schematic of the penetration model.

On solving the above partial differential equation, one obtains:

$$(c_{\mathrm{Ai}} - c)/(c_{\mathrm{Ai}} - c_{\mathrm{Ab}}) = \mathrm{erf}[z/\{2\sqrt{(D_{\mathrm{AB}}t)}\}] \tag{1.4}$$

If the process of mass transfer is a unidirectional diffusion and the surface concentration is very low: i.e. $c_{\mathrm{Ab}} \approx 0$; then the mass flux of solute A, given by N_{A} (kg/m^2 s) may be estimated by the following equation:

$$\begin{aligned} N_{\mathrm{A}} &= [\{-\rho D_{\mathrm{AB}}/(1 - c_{\mathrm{Ab}})\}](\partial c/\partial z)_{z=0} \\ &\approx -\rho(\partial c/\partial z)_{z=0} \end{aligned} \tag{1.5}$$

From the above two expressions, the rate of mass transfer at time t is given by the following equation:

$$N_{\mathrm{A}}(t) = [\sqrt{(D_{\mathrm{AB}}/\pi t)}](c_{\mathrm{Ai}} - c_{\mathrm{Ab}}) \tag{1.6}$$

And the mass transfer coefficient is given by

$$k_{\mathrm{L}}(t) = \sqrt{(D_{\mathrm{AB}}/\pi t)} \tag{1.7}$$

Moreover, the average mass transfer coefficient during a time interval $t_{\mathrm{c}}(t)$ may be obtained by integrating Eq. (1.4) as

$$k_{\mathrm{L,av}} = (1/t_{\mathrm{c}})\int_0^{t_{\mathrm{c}}} k(t)dt = 2\sqrt{(D_{\mathrm{AB}}/\pi t_{\mathrm{c}})} \tag{1.8}$$

Thus, from the above equation, the mass transfer coefficient is ***proportional*** to the square root of the diffusivity. This was first proposed by R. Higbie in 1935 and the theory is called the ***Higbie penetration theory***.

1.2.3 Absorption into a Quiescent Liquid

First, consider the case in which no chemical reaction occurring between the dissolved gas and the liquid [2]. The surface of the liquid first contacts the gas at time $t = 0$, and it may be assumed that, from that instance onward, the concentration in the plane of the surface is uniformly equal to A^* – this concentration corresponds to the solubility of the gas at the prevailing partial pressure above the surface of the liquid – and is assumed to be constant. If this gas were mixed with another gas of different solubility, or if there were a resistance the passage of gas across the interface, then the concentration at the surface may vary with time.

Further, it is assumed that the diffusion of dissolved gas into the liquid does not appreciably affect the temperature, or other physical properties of the latter. This is likely to be true only when the solubility of the gas is not very great, so that A^* represents a mole fraction much less than unity.

Under these special circumstances, the variation in time and space of the concentration a of dissolved gas in the liquid in the absence of reaction is governed by the diffusion equation:

$$D_A \partial^2 a/\partial x^2 = \partial a/\partial t \tag{1.9}$$

and the rate of transfer of dissolved gas across unit area, R_x of any plane parallel to the surface is

$$R_x = -D_A \partial a/\partial x \tag{1.10}$$

Here, x is the distance measured from the surface, where $x = 0$, and D_A is the diffusivity or diffusion coefficient of the dissolved gas. Hence, the rate of absorption of gas at any time is

$$R = -D_A(\partial a/\partial x)_{x=0} \tag{1.11}$$

The term $(\partial a/\partial x)_{x=0}$ is the concentration gradient at the surface and is a function of time.

Let the initial concentration of A be uniformly equal to A^0, and its concentration remote from the surface remains A^0. Then the solution of Eq. (1.9) with boundary conditions:

$$\begin{aligned} a = A^*, &\quad x = 0, \quad t > 0 \\ a = A^0, &\quad x > 0, \quad t = 0 \\ a = A^0, &\quad x = \infty, \quad t > 0 \end{aligned} \tag{1.12}$$

is

$$\begin{aligned} a - A^0 &= (A^* - A^0)\mathrm{erfc}\{x/2\sqrt{(D_A t)}\} \\ &= (A^* - A^0)[1 - \mathrm{erf}\{x/2\sqrt{(D_A t)}\}] \end{aligned} \tag{1.13}$$

Giving the distribution of concentration in the case where the initial concentration is A_0, and the function

$$\mathrm{erfc}\{x/2\sqrt{(D_A t)}\} = [1 - \mathrm{erf}\{x/2\sqrt{(D_A t)}\}] \tag{1.14}$$

is the error function of $x/2\sqrt{(D_A t)}$, and is defined by

$$\mathrm{erf}\{x/2\sqrt{(D_A t)}\} = (2/\sqrt{\pi})\int_0^{x/2\sqrt{(D_A t)}} \exp(-z^2)\,\mathrm{d}z \tag{1.15}$$

Values of the error function may be found in standard mathematical tables, etc. From Eqs. (1.11) and (1.13), it follows that

$$R = (A^* - A^0)\sqrt{(D_A/\pi t)} \tag{1.16}$$

Thus, the rate of absorption is infinite when the gas and liquid are first in contact, decreasing with time, and the amount Q absorbed by a unit area of surface, in time t, is given by

$$\begin{aligned} Q &= \int_0^t R\,\mathrm{d}t \\ &= 2(A^* - A^0)\sqrt{(D_\mathrm{A} t/\pi)} \end{aligned} \tag{1.17}$$

1.2.3.1 Absorption Accompanied by Chemical Reactions

If the dissolved gas reacts with the liquid, or with a substance dissolved in the liquid [2], then Eq. (1.9) should be replaced by

$$D_\mathrm{A}\partial^2 a/\partial x^2 = \partial a/\partial t + r(x,t) \tag{1.18}$$

in which $r(x, t)$ is the rate *per unit volume of liquid* at which the reaction is using up the solute gas at time t and at a distance x below the surface. This rate will depend on the local concentration of the gas, and of any other solute with which it reacts. For some cases, numerical and/or analytical solutions of the diffusion reaction equations are available.

It is assumed throughout that the temperature and the values of such as physico-chemical quantities as diffusivities, reaction-rate constants, and solubilities remain constant and uniform. Moreover, enhancement factors E may be computed which are the ratios of the amount which would be absorbed if there were no reaction, viz.

$$2(A^* - A^0)\sqrt{(D_\mathrm{A} t/\pi)}$$

1.2.3.2 Irreversible Reactions

1.2.3.2.1 First-Order Reactions

Here

$$r = k_1 a \tag{1.19}$$

in which k_1 is the first-order rate constant for the reaction. The rate of reaction of dissolved gas at any point is directly proportional to its concentration. Under these circumstances, the solution to Eq. (1.18), with boundary conditions (1.12), and with $A^0 = 0$, is [2, 4]:

$$\begin{aligned} a/A^* = {}& 1/2\exp\{-x\sqrt{(k_1/D_\mathrm{A})}\}\mathrm{erfc}[x/\{2\sqrt{D_\mathrm{A} t}\} - \sqrt{(k_1 t)}] \\ &+ 1/2\exp\{x\sqrt{(k_1/D_\mathrm{A})}\}\mathrm{erfc}[x/\{2\sqrt{D_\mathrm{A} t}\} + \sqrt{(k_1 t)}] \end{aligned} \tag{1.20}$$

so that

$$R = A^*\sqrt{(D_\mathrm{A} k_1)}[\mathrm{erf}\sqrt{(k_1 t)} + \exp(-k_1 t)/\sqrt{(\pi k_1 t)} \tag{1.21}$$

and

$$Q = A^*\sqrt{(D_\mathrm{A}/k_1)}\left[(k_1 t + 1/2)\mathrm{erf}\sqrt{(k_1 t)} + \sqrt{(k_1 t/\pi)}\exp(-k_1 t\right] \tag{1.22}$$

Thus, when k_1t is large, the distribution of concentration and absorption rate tend to limiting values and no longer change with time:

$$\text{for} \quad k_1t \gg 1$$

$$a/A^* = \exp\{-x\sqrt{(k_1/D_\text{A}}) \tag{1.23}$$

$$R = A^*\sqrt{(D_\text{A}k_1)} \tag{1.24}$$

and

$$Q = A^*\sqrt{(D_\text{A}k_1)}\{t + (1/2k_1)\} \tag{1.25}$$

The error in Eq. (1.25) is less than 3% when $k_1t > 2$.

When k_1t is large,

$$Q = tA^*\sqrt{(D_\text{A}k_1)} \tag{1.26}$$

to within 5% when $k_1t > 10$.

For short times of exposures, for $k_1t \ll 1$

$$R \approx A^*\sqrt{\{(D_\text{A}/\pi t)(1 + k_1t)} \tag{1.27}$$

$$Q \approx 2A^*\sqrt{\{(D_\text{A}t/\pi)(1 + k_1t/3)} \tag{1.28}$$

to within 5% when $k_1t < 0.5$.

The above equations form the basis of methods for measuring k_1 and $A^*\sqrt{D_\text{A}}$.

In practice, truly first-order irreversible reactions are seldom found. However, when the solute gas undergoes a reaction with a dissolved reactant, which is first order with respect to the concentration of the dissolved gas, then, under certain circumstances, the concentration of the reactant may be uniform and the reaction rate of the dissolved w order and the above equations do apply.

If the product of an irreversible first-order gas reaction has the same diffusivity as the dissolved gas, then its concentration P^* at the surface is given by Danckwerts (1967):

$$(P^*/yA^*) + 1 = \exp(-k_1t/2)[(1 + k_1t)I_0(k_1t/2) + k_1tI_1(k_1t/2)] = V_\text{A} \tag{1.29}$$

where y moles of product arise from the reaction of one mole of dissolved gas.

1.2.3.2.2 Instantaneous Reactions

In this case, the dissolved gas reacts instantaneously with a dissolved reactant. There is a plane underneath the surface where the concentration of both is zero, and the rate at which the two substances can diffuse to the reaction plane. The actual kinetics of the reaction are immaterial. The initial concentration of the reactant is uniformly B^0, and z moles of it react with each mole of dissolved gas.

The solution of the equations governing this case (and similar phenomena involving a moving boundary) has been given by Danckwerts [5]:

$$a/A^* = \left\{\text{erfc}[x/2\sqrt{(D_\text{A}t)}] - \text{erfc}\left(\beta/\sqrt{D_\text{A}}\right)\right\}/\text{erf}(\beta/\sqrt{D_\text{A}}), \quad 0 < x < 2\beta\sqrt{t} \tag{1.30}$$

$$a/A^* = 0, \quad x > 2\beta\sqrt{t} \tag{1.31}$$

$$b/B^0 = \left\{\mathrm{erf}\left[x/2\sqrt{(D_\mathrm{B}t}\right] - \mathrm{erf}(\beta/\sqrt{D_\mathrm{B}})\right\}/\mathrm{erfc}(\beta/\sqrt{D_\mathrm{B}}), \quad x > 2\beta\sqrt{t} \tag{1.32}$$

$$b/B^0 = 0, \quad 0 < x < 2\beta\sqrt{t} \tag{1.33}$$

$$R = \{A^*/\mathrm{erf}(\beta/\sqrt{D_\mathrm{A}})\}\sqrt{(D_\mathrm{A}/\pi)} = E_\mathrm{t}A^*\sqrt{(D_\mathrm{A}/\pi)} \tag{1.34}$$

$$Q = \{2A^*/\mathrm{erf}(\beta/\sqrt{D_\mathrm{A}})\}\sqrt{(D_\mathrm{A}t/\pi)} = 2E_\mathrm{t}A^*\sqrt{(D_\mathrm{A}t/\pi)} \tag{1.35}$$

where

$$E_\mathrm{i} = 1/\mathrm{erf}(\beta/\sqrt{D_\mathrm{A}}) \tag{1.36}$$

and β is defined by

$$\exp(\beta^2/D_\mathrm{B})\mathrm{erfc}(\beta/\sqrt{D_\mathrm{B}}) = (B^0/zA^*)\sqrt{(D_\mathrm{B}/D_\mathrm{A})}\exp(\beta^2/D_\mathrm{A})\,\mathrm{erf}(\beta/\sqrt{D_\mathrm{A}}) \tag{1.37}$$

Thus, the factor E_i is a function of $D_\mathrm{B}/D_\mathrm{A}$ and B^0/zA^*. Here a, b are the local concentrations of dissolved gas and reactant, respectively, and D_A, D_B *their* diffusivities. The reaction plane is at a depth of $2\beta\sqrt{t}$ beneath the surface. The quantity E_i is the factor by which the reaction increases the amount absorbed in a given time, as compared to absorption without reaction.

The concentration p of the product (assuming y moles to be formed from each mole of reacting gas) is

$$\begin{aligned} p = {} & yA^*\sqrt{(D_\mathrm{A}/D_\mathrm{P})}[\{\mathrm{erfc}(\beta/\sqrt{D_\mathrm{P}})\exp(-\beta^2/D_\mathrm{A})\}/ \\ & \{\mathrm{erfc}(\beta/\sqrt{D_\mathrm{A}})\exp(-\beta^2/D_\mathrm{P})\}], \quad 0 < x < 2\beta\sqrt{t} \end{aligned} \tag{1.38}$$

$$\begin{aligned} p = {} & yA^*\sqrt{(D_\mathrm{A}/D_\mathrm{P})}[\{\mathrm{erfc}(x/2\sqrt{D_\mathrm{P}})\exp(-\beta^2/D_\mathrm{A})\}/ \\ & \{\mathrm{erfc}(\beta/\sqrt{D_\mathrm{A}})\exp(-\beta^2/D_\mathrm{P})\}], \quad x > 2\beta\sqrt{t} \end{aligned} \tag{1.39}$$

where D_P is the diffusivity of the product.

When the diffusivities are equal:

$$p = yB^0/z, \quad 0 < x < 2\beta\sqrt{t} \tag{1.40}$$

If, in addition, one mole of reactant reacts with one mole of gas to produce one mole of product, then $y = z = 1$, and the concentration of product at the surface is the same as that of the reactant in the bulk.

When E_i is much greater than unity, then

$$E_\mathrm{i} = \sqrt{(D_\mathrm{A}/D_\mathrm{B})} + (B^0/zA^*)\sqrt{(D_\mathrm{B}/D_\mathrm{A})} \tag{1.41}$$

the error being of order $1/2E_\mathrm{i}$. When $D_\mathrm{A} = D_\mathrm{B}$,

$$E_\mathrm{i} = 1 + B^0/zA^* \tag{1.42}$$

for all values of the variables.

Under these conditions, the rate of absorption is equal to that of physical absorption of a gas of solubility $(A^* + B^0/z)$.

Remarks: In many cases, the reactions of the dissolved gases are so fast that they may be considered as instantaneous under all circumstances, for example:

(1) $H_2S + OH^- \rightarrow HS^- + H_2O$
(2) $H_2S + RNH_2 \rightarrow RNH_3^+ + HS^-$
(3) $NH_3 + HCl \rightarrow NH_4^+ + Cl^-$

Other reactions may have finite rates which may control the rate of absorption under certain circumstances, for example:

(4) $CO_2 + H_2O \rightarrow HCO_3^- + H^+$
(5) $CO_2 + OH^- \rightarrow HCO_3^-$
(6) $CO_2 + 2RNH_2 \rightarrow RNHCOO^- + RNH_3^+$
(7) $4Cu^+ + 4H^+ + O_2 \rightarrow 4Cu^{++} + 2H_2O$

In all these reactions, in which the reaction rates may be controlled by diffusion under some circumstances, and then the chemical steps in the reaction may be treated as though they were instantaneous. In general, irreversible reactions may be treated as instantaneous if the following condition is fulfilled:

$$(Q_0/2A^*)\sqrt{(\pi/D_A t)} \gg 1 + (B^0/zA^*) \tag{1.43}$$

in which Q_0 is the amount of gas which would be absorbed in time t if there were no depletion of reactant B in the neighborhood of the surface; if the condition is fulfilled, then the reactant B is entirely depleted in the neighborhood of the surface and the rate of reaction is only controlled by diffusion.

Worked Example 1.1

H_2S at 1 atm is absorbed into quiescent water and into a 0.1 M solution of monoethanolamine (MEA) at 25 °C. The reaction

$$H_2S + RNH_2 \rightarrow HS^- + RNH_3^+$$

may be taken to be instantaneous and irreversible. Calculate the amount of H_2S absorbed per cm^2 of surface in 0.1 s in water.

The diffusivity of H_2S in water is $1.48 \times 10^{-5}\ cm^2/s$. The solubility of H_2S is 0.10 g-mol/1 atm.

Solution

In water:

$$\begin{aligned} Q = 2A^*\sqrt{(D_A t/\pi)} &= 2 \times 0.1 \times 10^{-3} \times \sqrt{(1.48 \times 10^{-5} \times 0.1/\pi)} \\ &= 1.373 \times 10^{-7}\ \text{g-mol/cm}^2 \end{aligned}$$

1.2.3.2.3 Simultaneous Absorption of Two Reacting Gases

Consider the case of a mixture of two gases being absorbed simultaneously, in which each undergoes a second-order reaction with the same dissolved reactant [6]. As a typical example, this scenario may arise when a mixture of H_2S and CO_2 is absorbed by a solution of alkali amine. Here, the two solute gases are **A** and **B**, their concentrations at the surface, **A*** and **B***, will in general be different, as will their diffusivities $\boldsymbol{D}_{\mathbf{A}}$ and $\boldsymbol{D}_{\mathbf{B}}$, and their rate constants $\boldsymbol{k}_{\mathbf{A}}$ and $\boldsymbol{k}_{\mathbf{B}}$, governing their rates of reaction with the reactant **B**. The reactions are both supposed to be second order, so that the local rates of reaction are $\boldsymbol{k}_{\mathbf{A}}\boldsymbol{ab}$ and $\boldsymbol{k}_{\mathbf{B}}\boldsymbol{ab}$, respectively. Stoichiometrically:

$$\mathbf{A} + z\mathrm{B} \rightarrow \mathrm{P}$$

$$\mathbf{A} + z\mathrm{B} \rightarrow \mathrm{P}$$

The cases of a second-order reaction between A and B and an mth-, nth-order reaction between A and B will be considered in Chapter 3.

In the case of a second-order reaction, the necessary conditions will be discussed under Section 1.2.3.2.1 concentration where y moles of product arise from the reaction of one mole of dissolved gas. For large values of $k_1 t$, it approaches $2\sqrt{(k_1 t/\pi)}$.

1.2.4 Absorption into Agitated Liquids

In most commercial absorption mass transfer equipment such as plate or packed towers and columns [7], in almost all situations, one may and should consider the absorption of gases into liquids which are agitated vigorously so that the dissolved gases are transported from the surface to the interior by convective motion. Such agitations may occur in various ways, such as

1. The liquid may be running in a layer over a vertical surface or an inclined plane, and the flow may be laminar or turbulent, or ripples may develop and enhance the absorption rate by convective motion. Discontinuities on the surface may cause periodic mixing of the liquid layer along its flow (as in a packed column).
2. The gas may be blown through the liquid as streams of bubbles (as on a bubble plate).
3. The liquid may be agitated by a mechanical stirrer, which may also entrain bubbles of gas into the liquid.
4. The liquid may be sprayed.

The theory of diffusion and simultaneous chemical combination of several gases dissolving in a liquid and reacting near the interfaces had been discussed mathematically. The resultant set of nonlinear partial differential equations representing mass balances and corresponding to the penetration theory of mass transfer may be solved numerically. The chemical reaction rate expressions are second (or higher) order, corresponding to a bimolecular (or multi-molecular) mechanism. The results indicate that chemical reaction between two (or multiple) dissolved substances ***increases*** the rate of absorption of each by an amount (or amounts) that depend(s) on the ratio of solubilities, the reaction rate constant(s), and the diffusion coefficients. Mathematical solutions are presented for the simultaneous absorption of two gases in a liquid which contains a third component capable of reacting chemically with both of the dissolved gases. Based upon theoretical and experimental studies, one may express the rate of absorption of a gas in a liquid with which the gas reacts chemically in terms of diffusion and reaction kinetic mechanisms. The results are usually expressed by showing the ratio of absorption of the gas to the rate that would occur without the reaction, but with all other conditions held constant. This reaction rate enhancement ratio depends on:

- The reaction rate constant
- The time of exposure of the liquid surface to the gas
- The diffusion coefficients in the liquid
- Certain stoichiometric ratios.

The theoretical computation of such phenomena may be based on the assumption that diffusion and reaction take place in a laminar flow near the interface, the reaction rate per unit volume being so fast that only a small space in the liquid phase is sufficient to keep up with the diffusion of reactants to the reaction zone. With these simplifying assumptions, the resultant mathematical problem is that of solving the unsteady-state diffusion equation with a reaction term included. Thus, there will be as many different cases as there are orders of reaction and ways of bringing various numbers of reactants together.

The simplest problems are those in which linear partial differential equations are obtained, corresponding to first-order reactions of a single diffusing species after it dissolves in the liquid at the interface. Results of computations for both reversible and irreversible first-order reactions are available. Theoretical computations have been undertaken involving two dissolved substances: A and B, when A is initially in the gas, and B is a nonvolatile reagent initially present in the liquid. This situation is more complex than the linear problem; however, exact solutions have been obtained for fast reactions that are limited by diffusion of A and B to a reaction boundary that moves into the liquid as time elapses. When the reaction occurs at a finite rate, the reaction zone is diffuse, and no exact solutions have been obtained.

No theoretical calculations have been available for another physically interesting situation in which substances A and B are both gases that are brought into contact with a laminar layer of liquid in which both are soluble and within which they react with each other by a second-order chemical mechanism.

A typical practical example is the simultaneous absorption of CO_2 and NH_3 into water. These gases do ***not*** react in the vapor phase, but in the dissolved state they react with each other to form ammonium carbamate. The speed of the homogeneous reaction has been measured. As an additional example, gases containing both CO_2 and H_2S are sometimes washed with an alkaline liquid in which both gases dissolve and react, the two species competing for the same alkaline reagent.

However, it should not escape ones notice that these two examples are of fundamentally different types:

- In the former, a third substance is not involved, unless it is the solvent, which is present in a large excess and is not depleted by the reaction, or a homogeneous catalyst that is not consumed:
  - In the first example, the chemical equation is of the type: $A + B \rightarrow$
  - In the second example, a third substance is required for each dissolving gas to react, and its depletion from the solution near the interface ***limits*** the rate of absorption of *both* A *and* B. Then the chemical steps are typified by amounts that depend on the ratio(s) of solubilities, the various reaction rate constants, and the applicable diffusion coefficients. Mathematical solutions are presented for the simultaneous absorption of two gases in a liquid medium that contains a third component capable of reacting chemically with both of the dissolved gases.

    Based on the chemical steps beginning with

$$A + C \rightarrow$$

and, simultaneously:

$$B + C \rightarrow$$

A mathematical model for the simultaneous diffusion and reaction of two dissolved gases results in the following model differential equations.

A material balance on a differential element having dimensions $dx \times dz$ in the direction perpendicular to the interface and the direction of flow perpendicular to the interface and the direction of flow parallel to the interface, respectively, leads to a pair of nonlinear partial differential equations:

$$D_A \partial^2 A/\partial x^2 = u\partial A/\partial z + kAB \qquad (1.44A)$$

$$D_B \partial^2 B/\partial x^2 = u\partial B/\partial z + \nu kAB \qquad (1.44B)$$

where the last terms on the right-hand side of the two equations represent the rate of the homogeneous chemical reaction between substances A and B in the solution per unit volume of solution. The reaction is assumed to have the stoichiometry corresponding to the chemical equation:

$$A + \nu B \rightarrow \qquad (1.45)$$

and to be irreversible. Kinetically, it is assumed to be second order with respect to the two concentrations.

1.2.4.1 An Example of a First-Order Reaction

Consider a first-order irreversible reaction of a dissolved gas. It may be used to show how the effect of a chemical reaction may be calculated on the basis of three models. In this case, the local rate of reaction per unit volume is

$$r = k_1 a \qquad (1.46)$$

k_1 being the first-order reaction-rate constant, and a is the local content of dissolved gas.

1.2.4.2 The Film Model

The equation for the film model now takes the form

$$D_A \mathrm{d}^2 a/\mathrm{d}x^2 = k_1 a \quad \begin{cases} a = A^*, & x = 0 \\ a = A^0, & x = \delta \end{cases} \tag{1.47}$$

where $\delta = D_A/k_L$, k_L being the transfer coefficient the transfer for physical absorption. Thus,

$$a = (1/\sinh\sqrt{M})\{A^0 \sinh x\sqrt{(k_1/D_A)} + A^* \sinh[(D_A/k_L) - x]\sqrt{(k_1/D_A)}\} \tag{1.48}$$

where $M = D_A k_1/{k_L}^2$, and the absorption rate is

$$\underline{R} = -D_A(\mathrm{d}a/\mathrm{d}x)_{x=0} = k_L\{A^* - (A^0/\cosh\sqrt{M})\}\{\sqrt{M}/\tanh\sqrt{M}\} \tag{1.49}$$

Remarks:

(1) $\underline{R}$ is ***not*** directly proportional to $(A^* - A^0)$, as in physical absorption. This is generally the case when chemical reactions occur, and the value of A^0 is nonzero. Moreover, it is not generally appropriate to define a transfer coefficient as $R/(A^* - A^0)$, except in case of physical absorption only.

(2) The result expressed in Eq. (1.12) was first obtained by Hatta [8].

(3) When $\sqrt{M} \gg 1$, A^0 tends to zero, and Eq. (1.12) becomes

$$\underline{R} = A^*\sqrt{(D_A k_1)} \tag{1.50}$$

giving

$$E = \sqrt{(D_A k_1)}/k_L = \sqrt{M} \tag{1.51}$$

Here, E is the factor by which the chemical reaction *increases* the rate of absorption compared with merely physical absorption (with $A^0 = 0$ in both cases).

When $\sqrt{M} \gg 1$, the dissolved gases all react in the film and none diffuses in the unreacted state into the bulk of the liquid. Thus, the film thickness, or the value of k_L, is irrelevant and does not appear in the expression for $\underline{R}$.

For the Higbie model, one finds the expression for transient absorption, accompanied by irreversible first-order reaction.

1.3 The Mathematical Theory of Simultaneous Mass Transfer and Chemical Reactions

Consider the absorption of gases into liquids which are in a state of agitation such that the dissolved gases are transported from the surface to the interior by agitated convective motion [2]. The agitation may occur in one or more of several ways, including:

(1) The liquid may be blown through the liquid as a moving stream of bubbles, as, for example, on a bubble plate or in a sparged vessel.

(2) The liquid may be running in a layer over a vertical or an inclined surface, and the liquid flow may be turbulent (as, for example, in a wetted-wall column operating at a sufficiently high Reynolds Number, or ripples may develop and, thus, enhance the absorption process by convective motion.) Discontinuities in the surface may result in periodic mixing of the liquid layer in the course of its flow – as, for example, in a packed column, strings of discs, or strings of spheres.
(3) The liquid may be sprayed, as drops or jets, through the gas, as in a spray column of chamber.
(4) The liquid may be agitated by a stirrer which may also entrain bubbles of gas into the liquid.
(5) The liquid and gases may be interfaced in any physical contacting configurations and equipment.

1.3.1 Physical Absorption

In physical absorption, the gas dissolves in the liquid without reacting. The rate of absorption, found by experiment, is given by

$$\underline{R}a = k_{\mathrm{L}}a(A^* - A^0) \tag{1.52}$$

where

$\underline{R}$ is the average rate of transfer of gas per unit area
a is the area of interface between the gas and the liquid, per unit volume of the system
k_{L} is the "physical mass transfer coefficient"
A^* is the concentration of the dissolved gas corresponding to equilibrium with the partial pressure of the gas at the interface between gas and liquid
A^0 is the average concentration of dissolved gas in the bulk liquid.

In general, it is not possible to determine k_{L} and a separately by measurement of physical adsorption. For example, in a packed column, the fraction of the surface of packings which is effectively wetted is unknown; and in a system containing bubbles, the interfacial area is not known in general. Hence, the quantity that may be directly measurable by physical absorption measurements is the combined quantity $k_{\mathrm{L}}a$.

However, Eq. (1.52) has been established in many experimental investigations so that this equation would be predicted from basic principles whenever certain conditions are met – the main conditions are that the diffusivity and temperature at the surface (where the concentration is A^*) should not be very different from those in the bulk of the liquid, and that no chemical reaction occurs – so that all molecules of the dissolved gas are in the same conditions.

1.3.2 Chemical Absorption

1.3.2.1 Preliminary Remarks on Simultaneous Mass Transfer (Absorption) with Chemical Reactions

It is difficult to ascertain whether a solute, in fact, chemically reacts with a liquid or just interacts with it physically!

For the present purpose, a “physical” solution means that the dissolved molecules are indistinguishable, viz. not distinguishable as “unreacted” and “reacted” portions!

It has not escaped one’s attention that the effects of the hydrodynamics of agitated liquids may well have an important bearing on the issues at hand. Nevertheless, in the present context, it seems indeed useful to use some simplified models of the physical absorption process to describe and analyze the challenge at hand!

This approach will therefore proceed with a survey of some well-established models and proceed to describe the effect of chemical reactions on the mass transfer process!

In particular, the mass transfer models based upon:

(1) The Nernst one-film theory model,
(2) The Whitman two-film theory model,
(3) The Danckwerts surface renewal theory model,
(4) The Higbie penetration theory model,
(5) The boundary layer theory model.

A full presentation and discussion of these various approaches are presented in Chapter 3.

1.3.2.2 Some Solutions to the Mathematical Models of the Theory of Simultaneous Mass Transfer and Chemical Reactions

Some typical cases are:

(i) **Simultaneous Absorption of Two Reacting Gases** [2]:

Consider two gases being absorbed simultaneously, with each undergoing a second-order reaction with the same dissolved reactant. In practice, a typical example is the case of a mixture of H_2S and CO_2 being absorbed by a solution of amine or alkali.

Let A_1 and A_2 be the two solute gases, and their respective concentrations at the liquid surface be A_1^* and A_2^*, respectively, and their diffusivities be D_{A1} and D_{A2}, respectively, the rate constants k_1 and k_2 be governing the rates of their reactions with reactant B.

The reactions are both assumed to be of second order, so that the local rates of reaction are k_1ab and k_2ab, respectively.

Now, stoichiometrically, one may write:

$$\mathrm{A_1} + z_1\mathrm{B} \rightarrow \mathrm{P_1} \tag{1.53}$$

$$\mathrm{A_2} + z_2\mathrm{B} \rightarrow \mathrm{P_2} \tag{1.54}$$

Danckwerts reported that

(a) As $\sqrt{(k_2Bt)}$ approached ∞, the system approaches that for infinitely fast reaction of both solute gases, and an analytical solution is possible.
(b) In general, the effect of the presence of A_1 is to reduce the rate of absorption of A_2, and vice versa.

(ii) **Irreversible Reaction of General Order:**
Here, one may assume that the reaction rate is given by

$$r = k_{mn}(a)^m(b)^n \tag{1.55}$$

Reactions of such type, including
(a) The zero-order case: $m = 0$, $n = 0$, so that $(m+n) = 0+0 = 0$
(b) The first-order case: $m = 1$, $n = 0$, so that $(m+n) = 1+0 = 1$
(c) The second-order case: $m = 1$, $n = 1$, so that $(m+n) = 1+1 = 2$.
Defining the dimensionless quantity M by

$$M = [\pi/\{2(m+1)\}]k_{mn}(A^*)^{m-1}\,(B^0)^n t \tag{1.56}$$

Then,
(1) If $\sqrt{M} \gg (B^0/zA^*)\sqrt{(D_B/D_A)}$, then the rate of absorption is governed by diffusion alone, viz. the reaction may be considered as "instantaneous," and

$$R = -D_A(\partial a/\partial x)_{x=0} \tag{1.57}$$

applies. The term $(\partial a/\partial x)_{x=0}$ is the concentration gradient at the surface and is a function of time,
(2) If $\sqrt{M} \ll (B^0/zA^*)\sqrt{(D_B/D_A)}$, then the concentration of the reactant is practically uniform up to the surface of the liquid and equal to B^0. The reaction is then pseudo-mth order with $k_m = k_{mn}(B^0)^n$, and $r = k_m(a)^m$.

(iii) For the system H_2S and CO_2, if k_L is so small that

$$\sqrt{(D_A k_2 B^0)/k_L} \gg 1 + B^0/\left(2A_1^* + A_2^*\right) \tag{1.58}$$

where A_1^* and A_2^* are the surface concentrations of H_2S and CO_2, and the factor 2 is the stoichiometric factor for the reaction of CO_2 with NH_3 and the enhancement factors are:

$$E_{i1} \approx \left[1 + \left\{D_B B^0/(zA^* D_A + zA^* D_A\right\}\right]\sqrt{(D_{1A}/D_B)} \tag{1.59}$$

$$E_{i2} \approx \left[1 + \left\{D_B B^0/(zA^* D_A + zA^* D_A\right\}\right]\sqrt{(D_{2A}/D_B)} \tag{1.60}$$

These expressions show that the presence of A_2 diminishes E_i, and hence the rate of absorption of A_1, and vice versa.

1.3.2.3 Approximate Closed Form Solutions

In the mathematical analysis of simultaneous gas absorption and chemical reaction, a number of closed form solutions for special cases have been reported [9].

Example 1.1 ***Theory of the Stagnant Film of Finite Thickness – Slow First-Order Reaction***

In general, for a particular problem, the approach of using numerical analysis to obtain a useful solution is recommended. Much has been written on this methodology [9]. A reference to the latest standard collection is readily available in the most recent edition of "Perry's Chemical Engineers' Handbook," which should be a fruitful starting point.

If the reaction is not very fast compared with the diffusion rate, then the zone of reaction will not be restricted to a thin region, but will be spread throughout the liquid film, but will be spread throughout the liquid film. Consider the following derivation for the absorption and simultaneous slow irreversible reaction of a solute A, with a large excess of the solvent.

In this system, the solute diffuses through the gas film under the influence of the driving force ($p - p_i$). Upon entry into the liquid phase, it begins to diffuse toward the main body of the liquid and immediately starts to react with the dissolved substance B. Since the diffusing current of solute is being depleted as it diffuses into the liquid, the concentration gradient will be concave upward. The total rate of diffusion of reacted and unreacted forms of A is constant, since there is no accumulation of A in the film.

If the rate equation for the reaction is known, then the conditions of the process may be expressed mathematically. For example, assume that the reaction is of the first order and that the rate of elimination of A is proportional to the concentration of A at any point in time, viz.

$$-\mathrm{d}A/\mathrm{d}\theta = k_c cV \tag{1.61}$$

where

k_c is the specific reaction-rate constant,
c is the variable concentration of A, and
V is the liquid volume considered.

Next, consider a differential element, of unit cross-sectional area, and of thickness x_L.

The diffusion rate into this element will be

$$N_A = -D_A \mathrm{d}c/\mathrm{d}x \tag{1.62}$$

at $x = x$. The rate of diffusion out of this element, at $x = x + \mathrm{d}x$, will be

$$N_A = -D_A[\mathrm{d}c/\mathrm{d}x + (\mathrm{d}^2c/\mathrm{d}x^2)\mathrm{d}x] \tag{1.63}$$

The disappearance of A within the element, owing to reaction with B, is

$$\mathrm{d}A/\mathrm{d}\theta = -k_c c\,\mathrm{d}x \tag{1.64}$$

since the volume of the element is dx. The difference in diffusion rates in and out of the element must be equal to the rate of elimination of A by reaction with B, hence

$$D_A\,\mathrm{d}^2c/\mathrm{d}x^2 = k_c c \tag{1.65}$$

Now, assuming that k_c remains constant throughout the film, the solution of Eq. (1.65) may be expressed as

$$c = C_1\ \exp(a_0x) + C_2\ \exp(-a_0x) \tag{1.66}$$

where $a_0 = \sqrt{(k_c/D_A)}$.

Substituting the limits:

$$c = c_i \ \text{at}\ x = 0, \quad \text{and} \quad c = c_L \ \text{at}\, x = x_{La}$$

the constants C_1 and C_2 are obtained, and the solution takes the form:

$$c = [c_\mathrm{L}\ \sinh(a_0x) + c_\mathrm{i}\ \sinh\{a_0(x_\mathrm{L} - x)\}]/\sinh(a_0x_\mathrm{L}) \tag{1.67}$$

and for the case of $c_\mathrm{L} = 0$, Eq. (1.67) reduces to

$$c = c_\mathrm{i}\ \sinh\{a_0(x_\mathrm{L} - x)\}/\sinh(a_0x_\mathrm{L}) \tag{1.68}$$

Remark I:

(1) Equation (1.68) is mathematically analogous to the description of heat conduction along a fin that is maintained at a constant temperature at the base, with heat dissipation along the fin in proportion to the temperature profile maintained on the fin.

(2) By differentiating Eq. (1.67), the slope of the concentration curve is obtained as follows:

$$\mathrm{d}c/\mathrm{d}x = [a_0c_\mathrm{L}\ \cosh(a_0x) + a_0c_\mathrm{i}\ \cosh\{a_0(x_\mathrm{L} - x)\}]/\sinh(a_0x_\mathrm{L}) \tag{1.69}$$

(3) The rate of diffusion into the liquid may be obtained by multiplying the slope at $x = 0$ by the diffusivity D_A, viz.

$$\begin{aligned} N_\mathrm{A} &= -D_\mathrm{A}(\mathrm{d}c/\mathrm{d}x)_{x=0} \\ &= D_\mathrm{A}a_0[c_\mathrm{i}\cosh(a_0x_\mathrm{L}) - c_\mathrm{L}]/\sinh(a_0x_\mathrm{L}) \end{aligned} \tag{1.70}$$

(4) Similarly, the rate of diffusion of A into the main body of the liquid may be obtained by substituting $x = x_\mathrm{L}$:

$$\begin{aligned} N_\mathrm{A}' &= -D_\mathrm{A}(\mathrm{d}c/\mathrm{d}x)_{x=x_\mathrm{L}} \\ &= D_\mathrm{A}a_0\{c_\mathrm{i} - c_\mathrm{L}\cosh(a_0x_\mathrm{L} - x)\}/\sinh(a_0x_\mathrm{L}) \end{aligned} \tag{1.71}$$

(5) With respect to the solute A entering the liquid phase, the fraction F arriving at the main body of the liquid *without* reacting is

$$\begin{aligned} F &= N_\mathrm{A}'/N_\mathrm{A} \ \text{ and upon substituting from Eqs. (1.70) and (1.71)} \\ &= [\{c_\mathrm{i} - c_\mathrm{L}\cosh(a_0x_\mathrm{L} - x)\}/\{c_\mathrm{i}\cosh(a_0x_\mathrm{L}) - c_\mathrm{L}\}]\big|_{x=0} \\ &= \{c_\mathrm{L}\cosh(a_0x_\mathrm{L}) - c_\mathrm{i}\}/\{c_\mathrm{L} - c_\mathrm{i}\cosh(a_0x_\mathrm{L})\} \end{aligned} \tag{1.72}$$

Example 1.2 ***Theory of the Unsteady-State Absorption in a Stagnant Liquid – Slow First-Order Reaction***

At the ***initial*** exposure of a liquid to a gas during which the solute may accumulate in the liquid [9], an additional term should be added to Eq. (1.65)

$$D_\mathrm{A}\mathrm{d}^2c/\mathrm{d}x^2 = k_\mathrm{c}c$$

Remark II:

(1) Consider an elemental section make-up of the liquid phase near the interface, having a vertical side of unit cross section parallel near the interface, and a thickness dx. The rate of diffusion in and out of this liquid section are described

by the following two equations representing mass balances:

$$N_A = -D_A(\mathrm{d}c/\mathrm{d}x) \tag{1.73}$$

$$N_A = -D_A\{(\mathrm{d}c/\mathrm{d}x) + (\mathrm{d}^2c/\mathrm{d}x^2)\,\mathrm{d}x\} \tag{1.74}$$

while the net rate of disappearance per unit volume owing to reaction is given by

$$k_c c_A - k_{c'} c_B \tag{1.75}$$

where k_c *and* $k_{c'}$ are the rate constants for the forward and reverse reactions:

$$\mathrm{A} \leftrightarrow \mathrm{B} \tag{1.76}$$

(2) Now, at equilibrium, the opposing rates are equal:

$$K_c{}' = k_c/K \tag{1.77}$$

where K is the chemical equilibrium constant.

(3) The rate of depletion of A from the elemental section is $-(\partial c_A/\partial\theta)\,\mathrm{d}x$ in the unsteady state. Equating the rate of input of A by diffusion to the sum of the rates of output by diffusion, disappearance by reaction, and depletion, the result is

$$D_A(\partial^2 c_A/\partial x^2) = k_e c_A - (k_e/K)c_B + \partial c_A/\partial\theta \tag{1.78}$$

Similarly, a mass balance for B results in

$$D_A(\partial^2 c_A/\partial x^2) = (k_e/K)c_B - k_c c_A + \partial c_A/\partial\theta \tag{1.79}$$

(4) Should the concentration of B be eliminated and the diffusivities are assumed equal, the results is a *fourth-order* linear partial differential

$$\begin{aligned} &D(\partial^4 c_A/\partial x^4) - 2\partial^3 c_A/\partial\theta\partial x^2 - k_e\{1 + (1/K)\}(\partial^2 c_A/\partial x^2) \\ &\qquad + (1/D)\partial^2 c_A/\partial\theta^2 + (k_e/D)\{1 + (1/K)\}(\partial c_A/\partial\theta) \end{aligned} \tag{1.80}$$

(5) It is assumed that

(a) the product of the reaction is nonvolatile,
(b) the interfacial concentration of A is equal to the value in equilibrium with the gas, where the partial pressure of A is constant,
(c) the initial concentrations of A and B in the liquid before exposure to the gas are assumed to be uniformly equal to their equilibrium values,
(d) the body of liquid is considered to be infinite effectively.

Hence, correspondingly, the following boundary conditions are applicable:

(A) At $x = 0$: $c_A = c_i = p_A/H$
(B) At $x = 0$: $\partial c_B/\partial x = 0$
(C) At $\theta = 0$: $c_B = Kc_A = \{K/(1+K)\}c_0$, a constant
(D) At $x = \infty$: $c_B = Kc_A = \{K/(1+K)\}c_0$, a constant

where c_0 represents the sum of the initial values of c_A and c_B, which are assumed to be in equilibrium with each other.

(6) Since Eq. (1.80) is linear (with respect to the derivative terms) with simple boundary conditions, the Laplace transform method may be used to obtain its solutions, with the following results:

$$\{(K+1)c_{\mathrm{av}} - c_0\}/\{(K+1)c_{\mathrm{i}} - c_0\} = (3/\sqrt{\pi})\left\{\sqrt{(D_{\mathrm{L}}\theta/B_{\mathrm{F}}{}^2)}\right\} \times \{f(K, k_{\mathrm{c}}\theta)/(K+1)\} \tag{1.81}$$

where

$$\begin{aligned} f(K, k_{\mathrm{c}}\theta) = {} & K + 1 + [\pi K^5/\{4(K-1)(k_{\mathrm{c}}\theta)\}]^{1/2} \exp[k_{\mathrm{c}}\theta/\{K(K-1)\}] \\ & \times [\mathrm{erf}\{Kk_{\mathrm{c}}\theta/(K-1)\}]^{1/2} - \mathrm{erf}[k_{\mathrm{c}}\theta/\{K(K-1)\}^{1/2}] \\ & - [\{\pi K^3(K+1)\}/4k_{\mathrm{c}}\theta]^{1/2}\mathrm{erf}[\{(K+1)k_{\mathrm{c}}\theta\}/K]^{1/2} \end{aligned} \tag{1.82}$$

where $(K+1)c_{\mathrm{av}}$ is the average total concentration of solute in the liquid in both the reacted and the unreacted forms and c_{av} represents the average concentration of A after absorption if A and B were in chemical equilibrium at every point.

(7) Similarly, $(K+1)c_{\mathrm{i}}$ represents the total concentration of unreacted and reacted solute in the liquid if it were allowed to come to chemical and physical equilibrium with the gas.

(8) Using the following functional notations:

$$\exp(x) = \mathrm{e}^x \quad \text{and} \quad \mathrm{erf}(x) = (2/\sqrt{\pi})\int_0^q \mathrm{e}^{-p^2}\,\mathrm{d}p \tag{1.83}$$

(9) the latter being the error function.

  (i) For large values of $k_{\mathrm{c}}\theta$, the approximate equivalent of Eq. (1.81) is

$$\begin{aligned} f(K, k_{\mathrm{e}}\theta) = (1+K)\big[& 1 - (\pi^{1/2}/2)K\{K/(K+1)\}^{1/2}(k_{\mathrm{c}}\theta)^{-1/2} \\ & + [K^3/\{2(K+1)\}](k_{\mathrm{c}}\theta)^{-1}\big] \end{aligned} \tag{1.84}$$

  (ii) For small values of $k_{\mathrm{c}}\theta$ approximately, Eq. (1.84) simplifies to

$$f(K, k_{\mathrm{e}}\theta) = 1 + [\{K^{1/2}(K+1)^{3/2}(K-1)^2 - K^4 + 3K^2 - 2K\}/3(K-1)^2](k_{\mathrm{c}}\theta) \tag{1.85}$$

  (iii) For the irreversible reaction, viz., $K = \infty$

$$f(\infty, k_{\mathrm{e}}\theta) = 1/2\ \exp(-k_{\mathrm{e}}\theta) + \sqrt{(\pi/4)}\left\{(1 + 2k_{\mathrm{e}}\theta)/(k_{\mathrm{e}}\theta)^{1/2}\right\}\mathrm{erf}(k_{\mathrm{c}}\theta)^{1/2} \tag{1.86}$$

When these equations are applied to absorption from a gas in a falling liquid film, the time of exposure is that of the liquid surface, which may be calculated from the surface velocity:

$$\theta = Z/u_{\mathrm{s}} = (2/3)Z/u_{\mathrm{av}} \tag{1.87}$$

where Z is the height of the surface. By means of a mass balance on the liquid layer of thickness B_ν, the liquid film absorption coefficient k_{L} is obtained as follows:

$$u_{\mathrm{av}}B_\nu[(K+1)c_{\mathrm{av}} - c_0] = k_{\mathrm{L}}Z[(K+1)c_{\mathrm{i}} - c_0] \tag{1.88}$$

and

$$k_L Z/u_{av} B_\nu = [(K+1)c_{av} - c_0]/[(K+1)c_i - c_0] \tag{1.89A}$$

$$= (3/\sqrt{\pi})(D_L \theta/B\nu^2)^{1/2}\{f(K, k_c\theta)/(K+1)\} \tag{1.89B}$$

As before, in these equations:

- c_0 represents the concentration of total dissolved solute (both A and B forms) before exposure to the liquid surface and
- $(K+1)c_i$ represents the concentration of total dissolved solute, both A and B forms, in a liquid in phase equilibrium and reaction equilibrium with the gas – this latter quantity is not the actual solute concentration at the interface, where chemical equilibrium may not exist. It is the concentration which would be found in the usual static equilibrium experiment.

  The absorption coefficient k_L is defined in Eq. (1.88) on the basis of total dissolved-solute concentrations as a driving force. Comparing Eqs. (1.89A) and (1.89B) with the following equation (1.90), developed for pure physical adsorption:

$$k_L = \sqrt{(6/\pi)}\sqrt{(D_L u_{av}/Z)} \tag{1.90}$$

$$\text{viz.} \quad k_L Z/u_{av} B_r = (3/\sqrt{\pi})\sqrt{(D_L \theta/Br^2)} \tag{1.91}$$

  shows that $f(K, k_e\theta)/(K+1)$ is a multiplying factor which leads to the effect of chemical reaction on the coefficient for no reaction.
- Inspection of Eq. (1.85) shows that $f(K, k_e\theta)$ becomes equal to unity for the condition of a very unfavorable equilibrium ($K = 0$). Under this condition, the correction factor to the absorption coefficient becomes equal to 1, as expected.
- Also, $f(K, k_e\theta)$ becomes equal to unity when the equilibrium favors the production of B ($K > 0$), but the reaction is very slow ($k_e\theta \sim 0$).
- Equations (1.89A) and (1.89B) shows that under these conditions, the absorption coefficient is ***lower*** than that for purely physical absorption – owing to the fact that the solute dissolves at the interface in A form and does not react immediately: the interfacial concentration is only p_i/H, therefore, rather than $(K+1)(p_i/H)$, which is used to define k_L. The driving force causing diffusion is smaller, and the rate of absorption also smaller, owing to the reaction.
- When the reaction is fast: $k_e \rightarrow \infty$, Eq. (1.84) shows that $f(K, k_e\theta)$ approaches $(K+1)$ as a limiting value: the absorption coefficient then has its normal value, irrespective of K.

Example 1.3 *Theory of the Unsteady-State Absorption in a Stagnant Liquid – Rapid Second-Order, Irreversible Reaction*

For a chemical reaction occurring in the liquid, after the absorption of gaseous substance A, it may be stated as

$$\mathrm{A + B \rightarrow AB} \tag{1.92}$$

If the rate of absorption of A is sufficiently rapid, the rate may be limited by the rate at which B can diffuse from the liquid toward the gas–liquid interface – in order to react with A. Thus, the faster B is able to diffuse, the shorter the distance A will need to diffuse into the liquid to meet A. Thus, in contrast with the scenario for the first-order reaction:

$$\mathrm{A} \rightarrow \mathrm{C} \tag{1.93}$$

for which the absorption rate is independent of the concentration of B, in contrast to the second-order case wherein the absorption rate of A depends on the concentration of B.

When the reaction rate is extremely fast compared with the rate of diffusion of the reactants, the theory may be developed as shown here below.

In the absorption scenario, the following liquid layer has a uniform concentration of B when it is exposed to a gas containing A.

As A is absorbed, molecules of B which are near the interface are consumed in the reaction and are replenished by the diffusion of additional molecules of B from the main body of the liquid. As the reaction is assumed to take place instantaneously when A and B are brought together, regardless of the concentrations in the reaction zone, the point where A and B molecules meet each other will recede farther away from the interface. Hence, the absorption rate of A diminishes because the reacting molecules have to diffuse farther into the liquid to react! Thus, there is little or no opportunity for A to react until it arrives at the reaction zone at a distance x' from the interface. Hence, within the region $0 < x < x'$, the diffusion of A is represented by the second-order partial differential equation:

$$D_{\mathrm{A}} \partial^2 c_{\mathrm{A}} / \partial x^2 = \partial c_{\mathrm{A}} / \partial \theta \tag{1.94}$$

Similarly, component B does not react with A until B reaches the point $x = x'$; and for $x > x'$, the diffusion of B is governed by a similar second-order partial differential equation:

$$D_{\mathrm{B}} \partial^2 c_{\mathrm{B}} / \partial x_2 = \partial c_{\mathrm{B}} / \partial \theta \tag{1.95}$$

Moreover, for short times of exposure of the liquid surface, concentrations of A and B vary within a region near the interface, so that under these conditions, it may be assumed, without affecting the results significantly, that the liquid layer is infinitely deep: thus Eq. (1.95) applies within the region $x' < x < \infty$.

Sherwood and Pigford [10] showed, geometrically from the profiles of the concentration curves for A + B at times θ and $\theta + \mathrm{d}\theta$, that solutions of Eqs. (1.94) and (1.95) will be suitable if they can be made to satisfy the necessary boundary conditions and are as follows:

$$c_{\mathrm{A}} = A_1 + B_1 \operatorname{erf}[x / \{2\sqrt{(D_{\mathrm{A}} \theta)}\}] \tag{1.96}$$

$$c_{\mathrm{B}} = A_2 + B_2 \operatorname{erf}[x / \{2\sqrt{(D_{\mathrm{B}} \theta)}\}] \tag{1.97}$$

where the functional notation of Eq. (1.83) is used.

1.3.3 Numerical Solutions

In practice, when seeking numerical solutions for similar system sets of partial differential equations, it is much more straightforward to use numerical techniques such as techniques available in numerical analysis and/or solving in the R domain.

Fully worked out examples are provided in Chapters 3 and 4.

1.4 Diffusive Models of Environmental Transport

If one considers only the diffusive element, leaving out the reactive element, in a similar problem, a comprehensive collection of formulations have been systematically worked out by Choy and Reible [11], including:

* Diffusive Models of Environmental Transport
* Equilibria Within Environmental Phases
* Diffusion in Semi-infinite Systems
* Diffusion in Finite Layers
* Diffusion in Two-Layer Composite Systems
* Diffusion in Three-Layer Composite Systems
* Advective Diffusive Models
* Diffusion with Volatile Liquid Evaporation
* Diffusion with Time-Dependent Partition Coefficients
* Diffusion with Constant Flux Liquid Evaporation
* Some Typical Numerical Examples of Diffusive Models of Environmental Transport.

It certainly should not escape one's attention that, should there be reactive processes involved in any one of these cases, suitable reactive terms may be added to any of these models to provide the concomitant model description to reflect the simultaneous mass transfer and chemical reactions processes.

Further Reading

Emmert, R.E. and Pigford, R.L. (1963). In: *Perry's Chemical Engineers' Handbook*, 4e (eds. R.H. Perry, C.H. Chilton, and S.D. Kirkpatrick). *Section 14 'Gas Absorption and Solvent Extraction'*. New York: McGraw-Hill Book Company.

Roper, Hatch, and Pigford have obtained a theoretical solution, using graphic presentations, for the case where two absorbing gases react with one another.

Hatch and Pigford (*Ind. Eng. Chem., Fund. Quarterly* 1: 209 (1962)) described an experimental in which CO_2 and NH_3 simultaneously dissolved in water and reacted with one another. Their results thus confirmed the foregoing theory for the pseudo first-order case.