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The object of this column is to enhance our readers' collection of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and which elucidate difficult concepts. Please submit them to Professors James O. Wilkes and T. C. Papanastasiou, Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109.

REMOVAL OF CHLORINE FROM THE CHLORINE-NITROGEN MIXTURE IN A FILM OF LIQUID WATER

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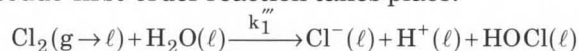
In industry there are many examples of absorption of a gas with or without chemical reaction in the liquid phase. In physical absorption, a particular gaseous component is removed from a gas mixture due to its larger solubility in the liquid phase solvent. The removal of butane and pentane from a refinery gas mixture by a heavy oil in the liquid phase is an example of physical absorption. In absorption with chemical reaction, the gaseous component to be removed transfers across the gas-liquid interface due to a difference in the bulk chemical potentials or concentrations in the two phases. The transferred gas then reacts with a liquid-phase component while simultaneously diffusing in the liquid phase mixture. The gas purification processes, such as removal of chlorine from nitrogen or air by means of water, removal of carbon dioxide from synthesis gas by means of aqueous solutions of hot potassium carbonate or monoethanolamine, and removal of H_2S and CO_2 from hydrocarbon cracking gas by means of ethanolamine or sodium hydroxide, are some examples of absorption with chemical reaction.



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PROBLEM STATEMENT

Chlorine is to be removed from a mixture of chlorine and nitrogen by absorption and reaction of chlorine with water in a falling liquid film, where a pseudo-first-order reaction takes place:



- Develop mathematical expressions describing two-dimensional concentration profiles of $Cl_2(A)$ in the liquid film, the total chlorine removal rate for the entire length of the film, and the mass transfer enhancement factor defined as the ratio of the actual rate of chlorine removal to the rate of chlorine removal in the absence of chemical reaction.
- Evaluate the two-dimensional chlorine concentration profile, the total chlorine removal rate, and the mass transfer enhancement factor for the following data:^[2]
 - System temperature: 24.5 C
 - Chlorine concentration in the liquid film at the gas-liquid interface: $C_{A0} = 0.1746 \times 10^{-5}$ mole cm^{-3}
 - Width of the liquid film: $w = 1.0$ cm
 - Thickness of the liquid film: $\delta = 0.008$ cm
 - Height of the falling liquid film: $L = 1.0$ cm
 - Pseudo-first-order reaction rate constant:

$$k_1''' = 13.6 \text{ s}^{-1}$$
 - Molecular diffusivity of chlorine (A) in the liquid solution: $D_A = 1.477 \times 10^{-5}$ $cm^2 \text{ s}^{-1}$

The chlorine removal process is to be carried out under isothermal and steady-state conditions by gently stirring the chlorine/nitrogen mixture as depicted in Figure 1.

PROBLEM SOLUTION

A sketch of the process is shown in Figure 1. Continuously flowing chlorine-nitrogen mixture is stirred and a film of liquid water falling along the vertical nonreactive plane wall is in contact with the gas phase. The gas mixture is at temperature, T , and pressure, P . The liquid phase concentration of chlorine at the gas-liquid interface can be determined for the evaluation of the numerical data using the methods given in References 3 and 4.

The solution^[1] to the momentum equation for the steady-state fully developed laminar flow gives an expression for the velocity, v_z , profile as

$$v_z(x) = v_m \left[1 - \left(\frac{x}{\delta} \right)^2 \right] \quad (1)$$

where

$$v_m = \frac{\rho g \delta^2}{2\mu} \quad (2)$$

and v_m = maximum velocity of liquid at the liquid-film surface

g = gravitational acceleration

ρ = liquid density

μ = absolute viscosity

To set up the differential model describing transport and consumption of the species A (Cl_2) in the liquid phase region, we follow the generally accepted approach given in Reference 1. The origin of the cartesian coordinate system x, y, z is located at the surface of the liquid film at its top end (see Figure 1). Species A is assumed to be transported in the x and z directions only. The concentration of the species A, C_A , is a function of both x and z coordinates. A mole balance for component A is applied over the spatial element in the liquid region shown in Figure 1. The

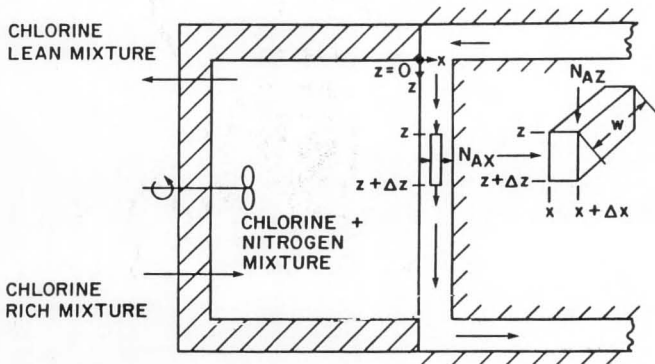


Figure 1. Sketch of the chlorine removal process by absorption and chemical reaction in the falling film of liquid water (not to scale).

resulting differential equation is

$$\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Az}}{\partial z} + k_1''' C_A = 0 \quad (3)$$

Under the assumption of negligible transport of species A by diffusion in the z direction relative to its transport by the liquid bulk flow, and no bulk flow in the x direction, N_{Az} and N_{Ax} are approximated by

$$N_{Az} = C_A v_z(x) \quad (4)$$

$$N_{Ax} = -D_A \frac{\partial C_A}{\partial x} \quad (5)$$

N_{Az} and N_{Ax} represent the molar fluxes of species A in the z and x directions, respectively.

Equations (1), (3), (4), and (5) are combined to result in

$$-D_A \frac{\partial^2 C_A}{\partial x^2} + v_m \left[1 - \left(\frac{x}{\delta} \right)^2 \right] \frac{\partial C_A}{\partial z} + k_1''' C_A = 0 \quad (6)$$

The required boundary conditions are:

$$\text{at } z=0 \quad C_A = 0 \quad \text{for } 0 < x \leq \delta \quad (7a)$$

$$\text{at } x=0 \quad C_A = C_{A0} \quad \text{for } 0 < z \leq L \quad (7b)$$

$$\text{at } x=\delta \quad \frac{\partial C_A}{\partial x} = 0 \quad \text{for } 0 < z \leq L \quad (7c)$$

If the region of the liquid film in the direction of the x coordinate, where molecules of the species A prevail, is thin relative to the liquid film thickness, then the liquid velocity in the downward direction in that region can be assumed to be close to the maximum velocity, v_m . This approximation results in the simplification of Eq. (6), making it suitable for obtaining an analytical solution. The simplified version of Eq. (6) is

$$-D_A \frac{\partial^2 C_A}{\partial x^2} + v_m \frac{\partial C_A}{\partial z} + k_1''' C_A = 0 \quad (8)$$

The boundary condition, Eq. (7c), is reduced to

$$x \rightarrow \infty, \quad C_A = 0 \quad \text{for } 0 \leq z \leq L \quad (9)$$

The assumption of constant velocity in Eq. (8) holds under the condition that chlorine is rapidly removed via chemical reaction in the liquid phase relative to its diffusion perpendicular to the gas-liquid interface.

Using the Laplace transform procedure,^[5,6] Eq. (8) is solved to obtain the following result:

$$\frac{C_A}{C_{A0}} = \frac{1}{2} \left[e^{-\sqrt{\beta} z} \operatorname{erfc} \left\{ \frac{1}{2} \sqrt{\frac{\alpha}{z}} - \sqrt{\frac{\beta}{\alpha}} z \right\} + e^{\sqrt{\beta} z} \operatorname{erfc} \left\{ \frac{1}{2} \sqrt{\frac{\alpha}{z}} + \sqrt{\frac{\beta z}{\alpha}} \right\} \right] \quad (10)$$

where

$$\alpha = \frac{v_m x^2}{D_A} \quad (11a)$$

$$\beta = \frac{k_1''' x^2}{D_A} \quad (11b)$$

Equation (10) describes the dimensionless concentration profile, C_A/C_{A0} , as a function of both x and z . Under the limit of $z \rightarrow \infty$ (i.e., sufficiently large z) so that erfc in the first term becomes $\text{erfc}(-\infty)$ and in the second term becomes $\text{erfc}(\infty)$, then Eq. (10) reduces to

$$\frac{C_A}{C_{A0}} = \exp(-\sqrt{\beta}) \quad (12)$$

The molar flux of species A into the liquid film at a z location is given by

$$N_{Ax} \Big|_{x=0} = -D_A \left(\frac{\partial C_A}{\partial x} \Big|_{x=0} \right) \quad (13)$$

The total removal rate of species A (i.e., of Cl_2) from the gas mixture is given by

$$W_A = w \int_{z=0}^{z=L} \left(N_{Ax} \Big|_{x=0} \right) dz$$

$$= w C_{A0} v_m \sqrt{\frac{D_A}{k_1'''} \left[\left(\frac{1}{2} + u \right) \text{erf}(\sqrt{u}) + \sqrt{\frac{u}{\pi}} e^{-u} \right]} \quad (14)$$

where

$$u = \frac{k_1''' L}{v_m} \quad (14a)$$

The expression for the removal rate of species A by its absorption in the absence of chemical reaction is obtained by substituting $k_1''' = 0$ in Eq. (14) and then applying the L'Hopital's rule to determine the resulting indeterminate limit. The result is given by

$$W_{A0} = w C_{A0} v_m \sqrt{D_A} \frac{L t}{k_1''' \rightarrow 0} \left(\frac{\frac{d}{dk_1'''} \left\{ \left(\frac{1}{2} + u \right) \text{erf}(\sqrt{u}) + \sqrt{\frac{u}{\pi}} e^{-u} \right\}}{\frac{d}{dk_1'''} \left\{ k_1'''^{1/2} \right\}} \right)$$

$$= w C_{A0} L \sqrt{\frac{4 D_A v_m}{\pi L}} \quad (15)$$

Finally, the mass transfer enhancement factor is given by

$$E_{mts} = \frac{W_A}{W_{A0}} = \left(\frac{\sqrt{\pi}}{2} \right) \left[\frac{\left(\frac{1}{2} + u \right) \text{erf} \sqrt{u} + \sqrt{\frac{u}{\pi}} e^{-u}}{\sqrt{u}} \right] \quad (16)$$

The second part of the problem is answered by obtaining the numerical data by means of a Fortran program that solves the above theoretical equations.

Error and complementary error functions were computed using the approximation technique from Reference 7. It is noted that $\text{erfc}(x) = 1 - \text{erf}(x)$. The resulting two-dimensional dimensionless concentration profiles of chlorine in the liquid film are shown in Figure 2. The calculated total chlorine removal rate is $W_A = 0.278 \times 10^{-7} \text{ mol s}^{-1}$, and the resulting mass transfer enhancement factor is $E_{mts} = 1.982$.

Validity of the assumption of constant velocity in Eq. (8) was verified by solving Eq. (6) numerically. Analytical solution of Eq. (8) and the numerical solution of Eq. (6) are compared in Figure 3 for two (z/L) locations.

DISCUSSION OF RESULTS

Figure 2 shows the profiles of the dimensionless concentration, C_A/C_{A0} , of chlorine as a function of the dimensionless penetration distance, x/δ , at a num-

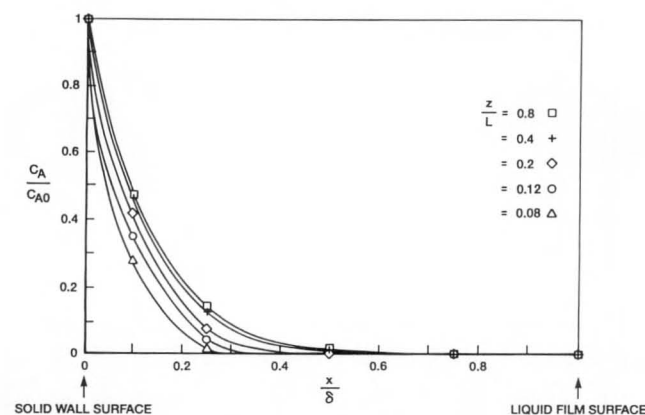


Figure 2. Two-dimensional concentration profiles of chlorine in the falling film of liquid water

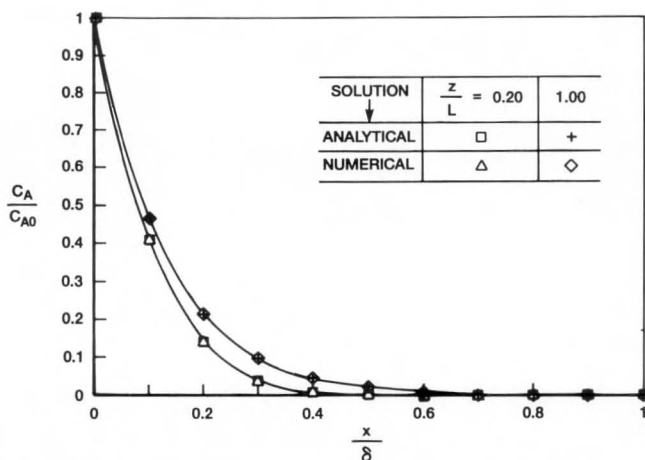


Figure 3. Comparison of the analytical solution of Eq. (8) with the numerical solution of Eq. (6).

ber of dimensionless depths, z/L . A rapid decrease in the chlorine concentration is interpreted in terms of its fast consumption via chemical reaction relative to its diffusion in the liquid phase. Agreement between the analytical solution of Eq. (8) and the numerical solution of Eq. (6) as seen in Figure 3 justifies the assumption of constant velocity in Eq. (8). The mass transfer enhancement factor value of 1.98 is indicative of about double the chlorine removal rate via its absorption without chemical reaction. The model predictions suggest that the continuously flowing liquid films can, indeed, be used for purification of gas mixtures, e.g., chlorine/nitrogen or air mixture, by absorption of trace species, e.g., chlorine, with chemical reaction in the liquid phase.

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REVIEW: Process Design

Continued from page 79.

the major types of equipment in the class, the basic operating principle, literature references, and sketches or photographs of the units. Short-cut sizing techniques and rules-of-thumb are used throughout the chapter for rough sizing. The major feature of the chapter is a set of tables which provide criteria for the preliminary specification of units within each equipment class. The selection tables are organized by principle of operation, applicable capacity range, important data to that class of equipment (i.e., particle size for crushing equipment), material compatibility, type of service, and any other criteria useful for differentiating alternatives within the class of equipment. Qualitative ranking of the units is provided when numerical comparisons are not appropriate for comparing equipment, such as past experience in the suitability of the unit for a particular

problem application. I tried to use the tables by selecting some units that I was particularly familiar with and found that they (and the text) provided enough basic information to describe the unit and give a size range. There is enough information to select a unit given the feed characteristics, but not enough information to do any analysis of the operation of the unit or detailed sizing.

The second section of the book (approximately one hundred and fifty pages) covers "Economic Analysis." Chapters cover capital and manufacturing cost estimation, economic optimization, and cash-flow analysis. The cost estimation techniques presented are adequate for a preliminary estimate. Figures provide capital cost estimates for different types of units, but there is no information about the error or spread of data used to create the figures. The chapter on cash-flow analysis (time value of money) is brief, and the coverage on the treatment of alternative investments could use more examples and discussion.

The final, brief, section is a single chapter on "Technical Reporting." There are many anecdotes to encourage the student to write effectively. It would have been useful to provide example outlines for different types of engineering design reports to give the student an idea of what information is expected, depending on the type of study being done.

After I finished reading the book, there were a number of things that troubled me. The *design process* is not emphasized as an iterative process that requires preliminary sizing and costing and then more detailed study and operations analysis (which may force changes in the original process concept). Little reference is made to modern computer packages that can do both the short-cut and the rigorous mass and energy balances (and sometimes the economics), and which allow the student to do a second pass at the design. The overall plant design is a set of chemical operations for which one must make decisions about unit alternatives as well as the process configuration itself. Process units interact through cycles so that design decisions in one unit can affect the operation, size, and economics of the rest of the plant. Some material and detailed examples on process configuration alternatives (process synthesis) would be useful for the student to see that different process concepts are possible.

If the instructor has a design course that is based on a well-defined case study, then the book provides reference material that would be useful for preliminary unit design and economic analysis. □