Steady State Absorption of a Sparingly Soluble Gas in an Agitated Tank with Simultaneous Irreversible First-order Reaction

E. N. LIGHTFOOT

University of Wisconson, Madison, Wisconsin

It is common practice to estimate volumetric mass transfer coefficients in gassed agitated tanks from the rates of absorption into liquids reacting chemically with the dissolving gas, for example the absorption of O_2 by aqueous sodium sulfite solutions containing a copper catalyst (*1, 2, 3*). The mass transfer coefficients are calculated by assuming steady state physical absorption into a liquid containing no dissolved gas. This calculation is reliable only if the chemical reaction is fast enough to maintain the concentration of dissolved gas near zero in the bulk of the solution but slow enough not to affect appreciably the concentration near the surfaces of dissolving gas bubbles.

No exact analysis of this situation is yet possible because of the complexity of the gas-absorption process; however a clearer understanding of the conditions required for the validity of this calculation method may be obtained by analysis of relatively simple model systems. This is done for first-order removal of dissolved gas and for two common models: absorption according to the penetration theory of Higbie (*4*) into bubbles with internal gas circulation and absorption through a hypothetical stagnant film of definite thickness completely surrounding the bubble. In each case it will be assumed that gas bubbles of reasonably uniform size and composition are evenly distributed about the tank and that no important gross variations in solution concentration or bubble velocity relative to the liquid occur. It will further be assumed that the gas is sparingly soluble, so that diffusion in the liquid obeys Fick's Law and interfacial concentration of gas is constant. Finally the system as a whole will be assumed to be at steady state, that is that the liquid in the tank is being maintained at constant over-all composition, or that the effect of rate of change of this composition is negligible. The latter will generally be true if the concentration of dissolved reactant is very large compared with the concentration of dissolving gas—a common situation.

CIRCULATING BUBBLES AND THE PENETRATION THEORY

Here the absorption is assumed to be to elements of liquid moving around the bubble from front to rear in accordance with Higbie's model (*4*) and maintaining their identity for a distance into the fluid greater than the effective penetration of dissolving gas during the time required for this journey. The differential equation and boundary conditions governing the rate of absorption are then

$$\mathfrak{D}\frac{\partial^2 c}{\partial x^2} = kc + \frac{\partial c}{\partial t} \tag{1}$$

at $x = 0,\ c = c_i$ for $t > 0$ (1*a*)

at $t = 0,\ c = c_0$ for all positive x (1*b*)

at $x = \infty,\ c = c_0 e^{-kt}$ for $t \geq 0$ (1*c*)

at any instant

$$-\mathfrak{D}\iint\limits_A \left(\frac{\partial c}{\partial x}\right)\bigg|_{x=0} dA = \iiint\limits_V kc\, dV \tag{1d}$$

where

A = total bubble surface area in tank, l^2

c = concentration of dissolved gas, $m./l^3$

c_i = concentration at the gas-liquid interface, assumed constant

c_0 = concentration of dissolved gas in a liquid element meeting the gas phase at the front of a bubble, that is, at the start of its journey around the bubble

$\mathfrak{D}$ = diffusivity of dissolved gas through the liquid, assumed constant, l^2/t

k = first-order reaction rate constant for removal of dissolved gas, t^{-1}

t = time measured for any liquid element from the time it first contacts a bubble

V = total volume of liquid in tank, l^3

x = distance measured outward from and normal to the bubble surface

Boundary condition [Equation (1*d*)] is a statement of steady state for the tank as a whole; its exact application requires a detailed knowledge of the flow pattern in the tank. Here an orderly flow of liquid around each bubble and complete mixing between bubbles will be assumed. Then Equation (1*d*) becomes

$$\int_0^{V/A} c(t_0, x)\, dx = \frac{V}{A}c_0 \tag{2}$$

where t_0 = time required for a liquid element to move completely around the bubble. Following the original suggestion of Higbie one can assume that

$$t_0 = D/v_t$$

where

D = diameter of bubble

v_t = bubble velocity relative to the fluid

With the aid of the first three boundary conditions Equation (1) may be integrated to give [see, for example, Equations 20(4) and 21(9) (*5*).]

$$\frac{c}{c_i} = \frac{1}{2}\left\{e^{-\xi}\,\mathrm{erfc}\left[\frac{\xi}{2\sqrt{\tau}} - \tau^{1/2}\right] + e^{\xi}\,\mathrm{erfc}\left[\frac{\xi}{2\sqrt{\tau}} + \tau^{1/2}\right]\right\} + \left(\frac{c_0}{c_i}\right)e^{-\tau}\,\mathrm{erf}\left[\frac{\xi}{2\sqrt{\tau}}\right] \tag{3}$$

where for convenience the dimensionless variables $\xi = x(k/\mathfrak{D})^{1/2}$ and $\tau = kt$ have been introduced.

Equations (2) and (3) can be combined to give an expression for c_0:

$$\frac{c_0}{c_i} = \frac{\mathrm{erf}\,(\tau_0)^{1/2} + \frac{1}{2}\left\{e^{\xi_0}\,\mathrm{erfc}\left[\frac{\xi_0}{2\sqrt{\tau_0}} + \tau_0^{1/2}\right] - e^{-\xi_0}\,\mathrm{erfc}\left[\frac{\xi_0}{2\sqrt{\tau_0}} - \tau_0^{1/2}\right]\right\}}{\xi_0\left[1 - e^{-\tau_0}\,\mathrm{erf}\left[\frac{\xi_0}{2\sqrt{\tau_0}}\right]\right] - \tau_0^{1/2}e^{-\tau_0}\left(\frac{2}{\pi^{1/2}}\right)[e^{-(\xi_0^2/4\tau_0)} - 1]} \tag{4}$$

Here

$$\xi_0 = (k/\mathfrak{D})^{1/2}(V/A)$$

$$\tau_0 = kD/v_t$$

Since the gas is sparingly soluble, the flux of gas at any point on the bubble surface is

$$N_G = -\mathfrak{D}\frac{\partial c}{\partial x}\bigg|_{x=0}$$

where N_G = moles of gas per area per unit time through interface and the average flux over the bubble surface

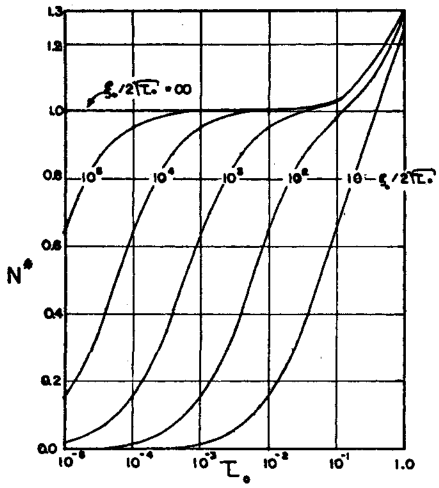

Fig. 1. Higbie model.

$$(N_G)_{avg} = \frac{1}{t_0}\int_0^{\tau_0} N_G\,dt \qquad (5)$$

Then from Equations (3) and (5)

$$(N_G)_{avg} = \frac{c_i(k\mathfrak{D})^{1/2}}{\tau_0}\left\{\left(\tau_0 + \frac{1}{2} - \frac{c_0}{c_i}\right)\cdot\operatorname{erf}\left({\tau_0}^{1/2}\right) + \frac{{\tau_0}^{1/2}}{\pi^{1/2}}e^{-\tau_0}\right\} \qquad (6)$$

or

$$N^* = \frac{1}{2}e^{-\tau_0} + \left(\tau_0 + \frac{1}{2} - \frac{c_0}{c_i}\right)\frac{\pi^{1/2}}{4\tau_0}\cdot\operatorname{erf}\left({\tau_0}^{1/2}\right) \qquad (7)$$

where

$$N^* = \frac{(N_G)_{avg}}{c_i}\left(\frac{\pi\tau_0}{4D}\right)^{1/2} \qquad (8)$$

Here N^* is the ratio of absorption rate in the presence of chemical reaction to the rate of physical absorption when the tank contains no dissolved gas. Thus this method of estimating mass transfer coefficients is valid only where N^* is one.

Figure 1 shows values of N^* for a wide range of values of $[\xi_0/2t_0^{1/2}]$ and t_0. It can be seen that for high enough values of $[\xi_0/2t_0^{1/2}]$ there is a plateau region, as suggested by Bernard, in which N^* is very nearly unity and independent of the chemical rate constant over a wide range. Such a situation would occur, for example, when (V/A) is large. However if the gas bubbles are concentrated in a small region of the tank, as from a single fine-bubble sparger, for example, Figure 1 could be misleading in that even distribution of bubbles has been assumed in this development.

STATIC FILM MODEL

It is assumed here that the gas bubbles are surrounded by static films, thin compared with the diameter of the bubbles, in which all the resistance to mass transfer is assumed to be concentrated and in which steady state is rapidly established. Film curvature and unsteady state may be taken into account if desired (*6*). Here

$$D\,\frac{\partial^2 c}{\partial x^2} = kc \qquad (8)$$

$$\text{at} \quad x = 0 \qquad c = c_i \qquad (8a)$$

$$\text{at} \quad x = \delta \qquad c = c_l \qquad (8b)$$

where δ is the film thickness. Then

$$\frac{c}{c_i} = \frac{(c_l/c_i)\sinh\xi + \sinh\left(\delta(k/\mathfrak{D})^{1/2} - \xi\right)}{\sinh\left(\delta(k/\mathfrak{D})^{1/2}\right)}$$

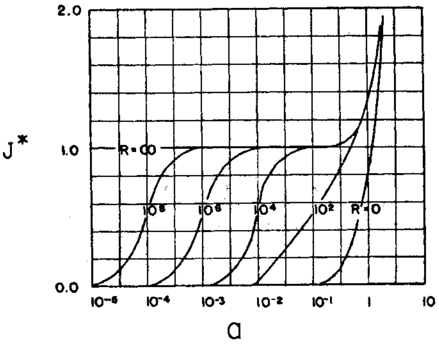

Fig. 2. Film model.

When one determines fluxes through the bubble-solution interface and outer film boundary and equates the rate of absorption through the outer film boundary with the rate of reaction in the bulk of the solution,

$$J^* = \frac{a}{\sinh a}\left[\cosh a - \frac{1}{\cosh a + aR\sinh a}\right] \qquad (9)$$

where

J^* = ratio of rate of absorption to rate of physical absorption to tank containing no dissolved gas

a = $\delta(k/\mathfrak{D})^{1/2}$

R = $V - A\delta/A\delta$ = ratio of volume of solution outside film to that inside film

In Figure 2 J^* is shown as a function of a and R. The behavior here is seen to be qualitatively similar to that for penetration theory model.

LITERATURE CITED

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BOOKS

The Properties of Gases and Liquids: Their Estimation and Correlation, Robert C. Reid and Thomas K. Sherwood, McGraw-Hill Book Company, Inc., New York (1958). 386 pages. $10.00.

This excellent book represents the investment of an immense quantity of work which has yielded excellent results. Reid and Sherwood's book is a critical summary of contemporary (1956) methods of calculating the common thermodynamic and transport properties of liquids and gases needed in design. The format of the book will appeal to the design engineer: the basic problems involved in calculating each property are outlined at the beginning of each chapter, then clear and concise descriptions of the selected methods are presented, and finally the best relations for various situations are recommended. In addition numerous sample calculations demonstrate the use of the equations, and an index of best methods for all properties covered is placed most advantageously at the beginning of the book. Thus it is easy to find, to understand, and to use the correlation sought.

The quality of this work stems from the authors' lucid understanding of the subject matter. Although not intended as a treatise upon aspects of physical chemistry, the text gives the reader an understandable, if abbreviated, description of the concepts involved. Hence the blunders which frequently appear in "plug-in" calculations are minimized. Since the decision to use a particular correlation rests upon the accuracy obtained for a given amount of work, statements of the expected accuracy are consistently given. These critical evaluations are based upon a vast body of calculations made by Reid and Sherwood in addition to the trials made by the various original authors. In particular, the authors stress the pitfalls of improper extrapolation of usage. Careful judgment is shown in the methods selected, most calculations being empirical but based upon theoretical considerations. The limitations of the empirical methods presented are emphasized, and tedious and often impractical theoretical methods are wisely avoided. When possible, tables and graphs of parameters appearing in these functions are located adjacent to their description. Thus most methods yield answers from a reasonably short calculation effort.

Reid and Sherwood have covered a vast field in surprisingly few pages, and hence omissions will appear to experts in the various fields covered (particularly the chapter on vapor-liquid equilibria). These limitations are more than compensated for by the general utility of the book; it is a must for design engineers and a necessary reference for students of applied physical chemistry and thermodynamics. The extensive documentation will appeal to researchers, as papers and reviews of particular merit are emphasized. Although the authors state that continued fundamental research and publication of physical properties will make their book needless, this reviewer

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