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Nomenclature

Bo	= Bond number $(=(\rho_l-\rho_g)gD^2/\sigma)$	[—]
D	= hole diameter	[m]
Fr^*	= modified Froude number $(=[\rho_g V_h^2/\{(\rho_l-\rho_g)gD\}]^{1/2})$	[—]
g	= gravitational acceleration	[m/s²]
H	= liquid depth	[m]
V_h	= gas velocity through hole	[m/s]
ρ_g, ρ_l	= density of gas and liquid	[kg/m³]
σ	= surface tension	[N/m]

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EXACT SOLUTION TO NO₂ ABSORPTION

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One of the most comprehensively investigated gas-liquid reaction systems is the absorption of NO₂ into an aqueous solution. Only in some limiting cases do analytical expressions exist to describe the mass transfer rate for absorption. The present paper describes an exact solution to the problem of absorbing NO₂ into an aqueous solution, in which case the NO₂ concentration is allowed to vary over a wide range.

Two reactions occur simultaneously in the liquid film:

$$2NO_2 \rightleftarrows N_2O_4 \qquad (I)$$

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3 \qquad (II)$$
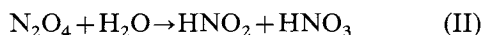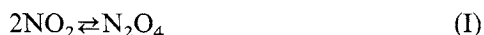
From a practical point of view, kinetic studies are performed in the presence of alkali or a buffer at a pH value above 7; alkali stabilizes HNO_2 due to nitrite ion formation.

For further details on the problem, it is refered to a series of papers by Aoki *et al.*,[1] and Komiyama and Inoue,[2,3] which probably represent the best up-to-date-knowledge on the subject.

The general conservation equations for the two reactions can be represented by a single expression:

$$2D_B\frac{d^2B}{dx^2}+D_A\frac{d^2A}{dx^2}-2k_{II}B=0 \qquad (1)$$

where A and B denote NO₂ and N₂O₄, respectively. Reaction (I) is instantaneous. Hence:

$$B=K_I A^2 \qquad (2)$$

The following variable transformations are introduced:

$$A^*=\delta A+2B \qquad (3)$$

$$\psi=dA^*/dx \qquad (4)$$

Equation (1) through (4) can then be manipulated to:

$$\psi \frac{d\psi}{dA^*} = \frac{k_{II}}{D_B\alpha}[2 + \alpha A^* - 2(1 + \alpha A^*)^{1/2}] \qquad (5)$$

where:

$$\alpha = 8K_I/\delta^2 \qquad (6)$$

The most workable boundary conditions are:

$$\begin{cases} A^* = A_0^* \\ \psi = -N/D_B \end{cases} \quad \begin{cases} A^* = 0 \\ \psi = 0 \end{cases} \qquad (7)$$

The first condition is obvious; the mass transfer rate is defined at $x = 0$ where $A^* = A_0^*$. Condition number two can be justified by the comparatively high reaction rates of the reactions involved. Aoki et al.[1] have shown the reactions to be in the fast regime, except for an extreme case which will be discussed at the end of this paper. By definition, all reactants are consumed in the film if the fast reaction regime prevails. Since no reaction occurs in the bulk, the bulk concentration of reactants must be zero. Furthermore, since no reactants leave the film, dA^*/dx must be zero at $x = l$ by definition. Lastly, since $A^* = 0$ in the bulk, it follows that $A^* = 0$ at $x = l$ to avoid reactants from being transferred from the film to the bulk. Hence, boundary condition number two is valid.

Integration of Eq. (5) and solving for N leads to:

$$N = \sqrt{k_{II}D_B/\alpha}\left[4A_0^* + \alpha A_0^{*2} \right.$$
$$\left. -\frac{8}{3\alpha}(1 + \alpha A_0^*)^{3/2} + \frac{8}{3\alpha} \right]^{1/2} \qquad (8)$$

A simplification can be obtained by defining the following dummy variable:

$$\xi = \frac{A_0\delta}{B_0 2} \qquad (9)$$

Considerable algebraic manipulations of Eq. (8) lead to:

$$N = 2\sqrt{k_{II}D_B\left(\frac{2}{3}\xi + 1\right)K_I A_0^2} \qquad (10)$$

Two limiting cases (mechanisms) can be obtained for high and low NO_2 concentration, in which case $\xi \to 0$ and $\xi \to \infty$, respectively:

$$N_1 = 2\sqrt{k_{II}D_B}K_I A_0^2 \qquad \frac{2}{3}\xi \ll 1 \qquad (11)$$

$$N_2 = 2\sqrt{k_{II}D_A K_I/3} A_0^{3/2} \qquad \frac{2}{3}\xi \gg 1 \qquad (12)$$

These expressions are well-known, e.g. Aoki et al.[1] Equation (10) holds for both mechanisms, as well as for the intervening transit region. Furthermore, it can easily be shown that:

$$N^2 = N_1^2 + N_2^2 \qquad (13)$$

Lastly, the extreme case of low NO_2 gas-phase concentration, i.e. below 5 ppm or so, in combination with a high physical liquid-side mass transfer coefficient has not been treated here. As shown by Aoki et al.,[1] the absorption follows the mechanism for physical absorption under such conditions.

Nomenclature

A	= liquid-phase concentration of NO_2; 0 indicates interfacial value; * denotes $\delta A + 2B$	$[\text{mol m}^{-3}]$
B	= liquid-phase concentration of N_2O_4; 0 indicates interfacial value	$[\text{mol m}^{-3}]$
D	= diffusion coefficient; A and B indicate NO_2 and N_2O_4, respectively	$[\text{m}^2\text{s}^{-1}]$
k_{II}	= rate constant for reaction (II)	$[\text{s}^{-1}]$
K_I	= equilibrium constant for reaction (I)	$[\text{mol}^{-1}\text{m}^3]$
l	= liquid film thickness	$[\text{m}]$
N	= mass transfer rate of $NO_2 + 2N_2O_4$; 1 and 2 indicate high and low NO_2 concentration, respectively	$[\text{mol m}^{-2}\text{s}^{-1}]$
x	= distance	$[\text{m}]$
α	= $8K_I/\delta^2$	$[\text{mol}^{-1}\text{m}^3]$
δ	= D_A/D_B	$[-]$
ξ	= $A_0\delta/(B_0 2)$	$[-]$
ψ	= dA^*/dx	$[\text{mol m}^{-4}\text{s}^{-1}]$

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