

GAS-LIQUID MASS TRANSFER WITH CHEMICAL REACTION IN BOTH PHASES

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A model is proposed in the paper enabling the rate of absorption to be calculated using the two-film theory. The absorption is accompanied by chemical reaction of the gas reactant in the liquid under conditions when the liquid phase reactant is also present in the gas phase. A simple approximative method of the calculation is proposed of the fluxes of both reacting components across the interface.

The usual assumption used in the formulation of mathematical models of mass transfer with chemical reaction in gas-liquid systems is that of a zero concentration gradient of the reacting component of the absorbent on the interface and hence unidirectional transport of mass across the interface from gas into liquid. In case when the absorbent contains a reactant of considerable vapour pressure under given conditions this assumption appears unrealistic since the reaction takes place in both phases and the mass transfer in both directions. An illustrative example of such types of reaction of practical importance is *e.g.* absorption of carbon dioxide in water solutions of ammonia. This problem in liquid-liquid systems has been examined recently by Rod¹ whose general formulation forms a starting point for this work. At the same time an attempt is made to find closer approximate solution for the reaction rate.

Consider a situation when a gas component A from phase G is transferred into phase L to react at finite rate with component B according to the scheme



Owing to its volatility the component B is present also in the gas phase and the reaction here proceeds according to the scheme



The fluxes of the components A and B in phases L and G are defined by the familiar formulas

$$J_A = \Phi_1 k_L c_{AL}^+, \quad (1)$$

$$J_B = \Phi_2 k_G c_{BG}^+. \quad (2)$$

The reactions in both phases are considered to be second-order and irreversible. From the viewpoint of the two-film theory of mass transfer with chemical reaction one can write:

For the liquid phase:

$$D_{AL} d^2 c_{AL}/dx^2 = k_{R1} c_{AL} c_{BL}, \quad (3)$$

$$D_{BL} d^2 c_{BL}/dx^2 = \nu k_{R1} c_{AL} c_{BL}. \quad (3)$$

$$x = 0, \quad c_{AL} = c_{AL}^+, \quad dc_{BL}/dx = J_B/D_{BL}; \quad (4)$$

$$x = \delta_1, \quad c_{AL} = 0, \quad c_{BL} = c_{BL}^0.$$

For the gas phase:

$$D_{AG} d^2 c_{AG}/dx^2 = k_{R2} c_{AG} c_{BG}, \quad (5)$$

$$D_{BG} d^2 c_{BG}/dx^2 = \alpha k_{R2} c_{AG} c_{BG}. \quad (6)$$

$$x = 0, \quad dc_{AG}/dx = J_A/D_{AG}, \quad c_{BG} = c_{BG}^+ \quad (7)$$

$$x = \delta_2, \quad c_{AG} = c_{AG}^0, \quad c_{BG} = 0.$$

Introducing dimensionless quantities as:

$$A_1 = c_{AL}/c_{AL}^+, \quad B_1 = D_{BL} c_{BL}/\nu D_{AL} c_{AL}^+, \quad Z_1 = x/\delta_1; \quad (8)$$

$$A_2 = c_{BG}/c_{BG}^+, \quad B_2 = D_{AG} c_{AG}/\alpha D_{BG} c_{BG}^+, \quad Z_2 = x/\delta_2.$$

Parameters:

$$M_1 = k_{R1} c_{BL}^0 \delta_1^2 / D_{AL} = k_{R1} c_{BL}^0 D_{AL} / k_L^2, \quad (9)$$

$$M_2 = k_{R2} c_{AG} \delta_2^2 / D_{BG} = k_{R2} c_{AG}^0 D_{AG} / k_G^2;$$

$$Q_1 = D_{BL} c_{BL}^0 / \nu D_{AL} c_{AL}^+, \quad Q_2 = D_{AG} c_{AG}^0 / \alpha D_{BG} c_{BG}^+;$$

$$R_1 = J_B / \nu J_A, \quad R_2 = J_A / \alpha J_B,$$

Eqs (3)–(7) may be written in dimensionless forms as:

$$d^2 A_1/dZ_1^2 = (M_1/Q_1) A_1 B_1, \quad d^2 A_2/dZ_2^2 = (M_2/Q_2) A_2 B_2; \quad (10a,b)$$

$$d^2 B_1/dZ_1^2 = d^2 A_1/dZ_1^2, \quad d^2 B_2/dZ_2^2 = d^2 A_2/dZ_2^2, \quad (11a,b)$$

$$Z_1 = 0, \quad A_1 = 1, \quad dB_1/dZ_1 = R_1 \Phi_1; \quad (12)$$

$$Z_1 = 1, \quad A_1 = 0, \quad B_1 = Q_1;$$

$$Z_2 = 0, \quad A_2 = 1, \quad dB_2/dZ_2 = R_2 \Phi_2; \quad (13)$$

$$Z_2 = 1, \quad A_2 = 0, \quad B_2 = Q_2.$$

For the reaction factors one has from Eqs (1) and (2):

$$\Phi_1 = J_A \delta_1 / D_{AL} c_{AL}^+; \quad \Phi_2 = J_B \delta_2 / D_{BG} c_{BG}^+. \quad (14)$$

From the above equations and the expressions for the fluxes:

$$J_A = -D_{AL}(dc_{AL}/dx)_{x=0}, \quad J_B = -D_{BG}(dc_{BG}/dx)_{x=0}, \quad (15)$$

it follows

$$\Phi_1 = -(dA_1/dZ_1)_{Z_1=0}, \quad \Phi_2 = -(dA_2/dZ_2)_{Z_2=0}. \quad (16)$$

In view of the formal similarity of the expressions for both phases the solutions will be developed for the liquid phase only:

On integrating Eq. (11a) and making use of the boundary conditions (12) and (13) one obtains for the dimensionless concentration of the component B_1 in the liquid film

$$B_1 = A_1 + Q_1 - \Phi_1(R_1 + 1)(1 - Z). \quad (17)$$

Substituting in Eq. (10a) a non-linear differential equation is obtained necessitating a numerical solution:

$$(d^2 A_1/dZ_1^2) = (M_1/Q_1) A_1 [A_1 + Q_1 - \Phi_1(R_1 + 1)(1 - Z_1)]. \quad (18)$$

A simple approximate solution is obtained by the following procedure: The profile of the component A_1 in the film assumed in the form¹:

$$A_1 = \sinh \Gamma(1 - Z_1)/\sinh \Gamma ; \quad (19)$$

Substituting the last expression in Eq. (18) and after some arrangement one obtains for Γ the following:

$$\Gamma = \left\{ \frac{M_1}{Q_1} \left[\frac{\sinh \Gamma(1 - Z_1)}{\sinh \Gamma} + Q_1 - \Phi_1(R_1 + 1)(1 - Z_1) \right] \right\}^{1/2}. \quad (20)$$

On differentiating Eq. (19) and combining with the definition of the reaction factor, Eq. (18), one obtains the well-known formula:

$$\Phi_1 = \Gamma/\tanh \Gamma. \quad (21)$$

The reaction factor is computed from Eqs (20) and (21) in an iterative fashion. It is assumed that the solution satisfies Eq. (18) in an arbitrary point Z_1 from the interval 0–1 taken conveniently so as to simplify the form of Eq. (18). It may be shown that the choice of *e.g.* $Z_1 = 0$, as it is usual, *i.e.*

$$B_1 = 1 + Q_1 - \Phi_1(R_1 + 1) \quad (22)$$

does not give, in principle, realistic estimates of the reaction factor (for B_1 vanishing one gets $\Phi = 1$). It turns out that an essential prerequisite is to take the point Z_1 from the region of the maximum of the slope of the concentration profile of A_1 in the liquid film; a correct estimate of the course of the concentration of A_1 is a crucial factor for a correct estimate of the whole concentration profile of the components. The choice of Z_1 approaching unity leads in the limit to incorrect solutions $\Phi_1 \rightarrow M_1^{1/2}$ which is inconsistent with the exact solution, particularly not for high M . As a suitable point for matching we took

$$Z_1 = 1/3\Phi_1. \quad (23)$$

Substituting Eq. (23) into (19) and (20) one can compute in a simple iterative manner the reaction factor from Eq. (21).

To illustrate the routine a numerical solution for the case¹ $M_1 = 100$, $Q_1 = 10$, $R_1 = 1$ $\Phi_{1,e} = 4.69$ was compared with the approximate solution given by Eqs (19)–(21). The latter gave the value $\Phi_1 = 4.62$, *i.e.* with an error of 1.5%. Even for this relatively favourable combination of the parameters = M_1 , Q_1 , R_1 (from the viewpoint of comparison of the two types of the solution) the error with the choice according to Eq. (22) is greater: 4.3%. In other cases the approximate solution with the aid of Eq. (23) does not deviate from the numerical values by more than 5%.

The above equations were formulated so as to make both phases formally similar, *i.e.* partial pressures for the gas phase were replaced by mol/unit of volume concentration units. As a consequence of the chemical reaction in both phases the equilibrium concentrations on the interface, c_{AL}^+ and c_{BG}^+ , depend on the solution of the concentration profile by the above method in the points $Z_1, Z_2 = 0$.

Then

$$c_{AL}^+ = H_A RT c_{AG,i}, \quad c_{BG}^+ = c_{BL,i} / H_B RT, \quad (24)$$

where the concentrations at the interface, $c_{AG,i}$ and $c_{BL,i}$, follow from the equation

$$1 + Q_2 - \Phi_2(R_2 + 1) = D_{AG} c_{AG,i} / D_{BG} [c_{BL,i} / H_B RT], \quad (25)$$

$$1 + Q_1 - \Phi_1(R_1 + 1) = D_{BL} c_{BL,i} / D_{AL} H_A RT c_{AG,i}. \quad (26)$$

The following equations complete the set of equations necessary for an estimate of absorption rates

$$J_A = \Phi_1 k_L (H_A RT) c_{AG,i} \quad (27)$$

$$J_B = \Phi_2 k_G (c_{BL,i} / H_B RT), \quad (28)$$

$$\Phi_1 = \Phi_1(M_1, Q_1, R_1), \quad (29)$$

$$\Phi_2 = \Phi_2(M_2, Q_2, R_2), \quad (30)$$

$$M_1 = k_{R1} c_{BL}^0 D_{AL} / k_L^2, \quad (31)$$

$$M_2 = k_{R2} c_{AG}^0 D_{BG} / k_G^2, \quad (32)$$

$$Q_1 = D_{BL} c_{BL}^0 / \nu D_{AL} H_A RT c_{AG,i}, \quad (33)$$

$$Q_2 = D_{AG} c_{AG}^0 / \alpha D_{BG} c_{BL,i} / H_B RT, \quad (34)$$

$$R_1 = J_B / \nu J_A, \quad (35)$$

$$R_2 = J_A / \alpha J_B, \quad (36)$$

for the unknowns $c_{AG,i}, c_{BL,i}, Q_1, Q_2, M_1, M_2, R_1, R_2, \Phi_1, \Phi_2, J_A, J_B$.

LIST OF SYMBOLS

A_1	dimensionless concentration of A in liquid, Eq. (10)
A_2	dimensionless concentration of B in gas, Eq. (10)
B_1	dimensionless concentration of B in liquid, Eq. (10)
B_2	dimensionless concentration of A in gas
c_{AG}	concentration of A in the bulk of gas (mol/m ³)
c_{BL}^0	concentration of B in the bulk of liquid (mol/m ³)
c_{AG}^0	concentration of A in gas film (mol/m ³)
c_{BG}^0	concentration of B in gas film (mol/m ³)
c_{AL}	concentration of A in liquid (mol/m ³)
c_{AL}^+	equilibrium concentration of A in liquid at the interface (mol/m ³)
c_{BG}^+	equilibrium concentration of B in gas at the interface (mol/m ³)
$c_{AG,i}$	concentration of A in gas at the interface, Eq. (25) (mol/m ³)
$c_{BL,i}$	concentration of B in liquid at the interface, Eq. (26) (mol/m ³)
D_{AL}	diffusion coefficient of A in liquid (m ² /s)
D_{BL}	diffusion coefficient of B in liquid (m ² /s)
D_{AG}	diffusion coefficient of A in gas (m ² /s)
D_{BG}	diffusion coefficient of B in gas (m ² /s)
H_A	Henry constant for A (mol/m ³ at)
H_B	Henry constant for B (mol/m ³ at)
J_A	mole flux of A (mol/m ² s)
J_B	mole flux of B (mol/m ² s)
k_L	liquid-side mass transfer coefficient (m/s)
k_G	gas-side mass transfer coefficient (m/s)
k_{R1}	reaction rate constant in liquid (m ³ /mol s)
k_{R2}	reaction rate constant in gas (m ³ /mol s)
M_1, M_2	parameters, Eq. (9)
Q_1, Q_2	parameters, Eq. (9)
R_1, R_2	parameters, Eq. (9)
R	gas constant (at m ³ /mol K)
T	absolute temperature
x	distance from interface
Z_1	dimensionless distance on liquid side
Z_2	dimensionless distance on gas side
Φ_1	liquid side reaction factor
Φ_a	gas side reaction factor
ν	stoichiometric coefficient
α	stoichiometric coefficient
δ_1	thickness of liquid film (m)
δ_2	thickness of gas film (m)
Γ	parameter, Eq. (20)

REFERENCES

V. Rod: This Journal 38, 3228 (1973).

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