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THE EFFECT OF INSTANTANEOUS CHEMICAL REACTIONS AT THE INTERFACE ON DIFFUSION IN A COMPOSITE MEDIUM

J. SZEKELY
Department of Metallurgy, Royal School of Mines, Imperial College, London

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Abstract—The paper considers the effect of instantaneous chemical reactions at the interface on diffusion in an infinite composite medium.

On the assumption of uniform initial values expressions are derived for the "fields" of the concentrations and for the fluxes crossing the interface in the case of second order reversible and irreversible reactions. The results allow extension of the bubble-stirred interface model to systems with instantaneous surface reaction and may be relevant for the interpretation of some slag–metal interactions in steelmaking processes.

NOMENCLATURE

A, B,	reactants;
A_i, A_j,	constants in equations (9) and (10) referring to phases 1 and 2, respectively;
C,	instantaneous molar concentration;
$\bar{C}$,	uniform bulk concentration (molar);
D,	diffusivity;
K,	equilibrium constant;
K',	constant, defined in equation (22b);
N,	molar flux;
$N(t)$,	instantaneous flux (molar);
$\bar{N}(t)$,	time averaged flux (molar) defined in equation (20);
t,	time;
t_e,	time interval, [1];
x,	distance from interface;
Z,	reaction product;
α,	defined in equation (34);
β,	defined in equation (35);
$\phi(N_i, N_j)$,	flux boundary condition;
$\psi(C_i, C_j)$,	boundary condition relating concentrations.

Subscripts

1,	refers to substance A;
2,	refers to substance B;
3,	refers to substance Z;
i, j,	refer to phases 1 and 2 respectively.

INTRODUCTION

IN A PREVIOUS paper [1] a model was proposed for transport across the bubble-stirred interface of two immiscible liquids. Heat transfer and mass transfer, in the absence of chemical reactions, were considered and expressions were derived for point values and time averaged values of the flux crossing the interface. The mathematical problem involved was essentially diffusion or heat conduction in an infinite composite medium for which solutions were readily available in the literature [2, 3].

As one practical application of the model is the interpretation of some slag–metal interactions it is of interest to examine the effect of an instantaneous chemical reaction occurring at the interface on the mass-transfer rate.

Here the mathematical problem is to solve the diffusion equation for an infinite composite medium with an instantaneous chemical reaction at the interface. In the following, solutions for this general problem will be given, together with a discussion on the possible practical application of the results.

Three cases will be considered:

(*a*) Instantaneous irreversible reaction of the form

$$A + mB \rightarrow \text{PRODUCTS}$$

where substance A is contained only in phase 1, substance B only in phase 2.

(*b*) Second order instantaneous reversible reaction where transport of the products is unimportant such that

$$A + B \rightleftharpoons Z; \quad (A)(B) = K'$$

where A and B are contained only in phase 1; and phase 2 is made up of pure Z.

(*c*) General case of a second order instantaneous reversible reaction of the form

$$A + B \rightleftharpoons Z$$

where A is contained only in phase 1 and B and Z are contained only in phase 2.

General formulation

Consider two immiscible liquid phases (1) and (2) extending from $x = 0_{(+)}$ to $x = \infty$ and $x = 0_{(-)}$ to $x = -\infty$ respectively.

In the absence of bulk motion and for small fluxes of the diffusing substance the conservation of any species can be written as [2].

$$D_i \frac{\partial^2 C_i}{\partial x^2} = \frac{\partial C_i}{\partial t}, \text{ for } x > 0 \tag{1}$$

and

$$D_j \frac{\partial^2 C_j}{\partial x^2} = \frac{\partial C_j}{\partial t}, \text{ for } x < 0. \tag{2}$$

Subscripts i and j refer to any species in phases 1 and 2 respectively. Boundary conditions common to all the problems discussed in this paper are as follows:

$$C_i = \bar{C}_i, \quad \text{at} \quad t = 0 \tag{3}$$

$$C_j = \bar{C}_j, \quad \text{at} \quad t = 0 \tag{4}$$

$$C_i \rightarrow \bar{C}_i, \quad \text{for} \quad x \rightarrow \infty \tag{5}$$

$$C_j \rightarrow \bar{C}_j, \quad \text{for} \quad x \rightarrow -\infty. \tag{6}$$

The boundary conditions relating fluxes, i.e.

$$\phi(N_i, N_j) = 0, \text{ at } x = 0 \tag{7}$$

and concentrations, i.e.

$$\psi(C_i, C_j) = 0, \text{ at } x = 0 \tag{8}$$

are essentially that the respective fluxes follow the stoichiometric relationship and that equilibrium exists at the interface. However, the actual algebraic expressions are different for cases (*a*), (*b*), (*c*) and will be given under the appropriate section headings.

It can be shown that for cases (*a*), (*b*), and (*c*), the solutions of (1) and (2) can be found in the form:

$$\bar{C}_i = C_i + A_1 \operatorname{erfc} \frac{x}{2\sqrt{(D_i t)}} \tag{9}$$

and

$$\bar{C}_j = \bar{C}_j + A_j \operatorname{erfc} \frac{|x|}{2\sqrt{(D_j t)}} \tag{10}$$

where A_i and A_j are constants to be determined from the boundary conditions.

The rest of the paper is devoted to the evaluation of these constants for the various cases considered, and to a discussion of the resultant expressions.

(*a*) *Irreversible reaction*

$$A + mB \rightarrow \text{PRODUCTS}$$

such that substance A is contained only in phase 1 and substance B only in phase 2.

Let C_1 and C_2 denote concentrations in phases 1 ($x > 0$) and 2 ($x < 0$) respectively.

Irreversible instantaneous reaction implies that at the interface A and B cannot coexist.

$$\text{i.e.} \quad \psi(C_i, C_j) = C_1 C_2 = 0, \text{ at } x = 0. \tag{11}$$

The boundary condition relating fluxes, i.e. (N_i, N_j) can be written as:

$$D_1 \frac{\partial C_1}{\partial x} = -m D_2 \frac{\partial C_2}{\partial x}, \text{ at } x = 0. \tag{12}$$

Substitution of (9) and (10) into (11) and (12) will allow evaluation of A_1 and A_2. Thus after some arithmetic we have:

$$C_1 = \bar{C}_1 - \tfrac{1}{2} \left\{ m \left(\frac{D_2}{D_1}\right)^{1/2} (\bar{C}_2 + \bar{C}_1) + \left[m \left(\frac{D_2}{D_1}\right)^{1/2} \bar{C}_2 - \bar{C}_1 \right] \right\} \operatorname{erfc} \frac{x}{2\sqrt{(D_1 t)}} \tag{13}$$

and

$$C_2 = \bar{C}_2 - \frac{1}{2m}\left(\frac{D_1}{D_2}\right)^{1/2}\left\{\left[m\left(\frac{D_2}{D_1}\right)^{1/2}\bar{C}_2 + \bar{C}_1\right] \pm \left[m\left(\frac{D_2}{D_1}\right)^{1/2}\bar{C}_2 - \bar{C}_1\right]\right\}\operatorname{erfc}\frac{|x|}{2\sqrt{(D_2 t)}}. \quad (14)$$

Considering that both C_1 and C_2 must be positive it follows that when

$$m\left(\frac{D_2}{D_1}\right)^{1/2}\bar{C}_2 > \bar{C}_1$$

equations (13) and (14) can be written as:

$$C_1 = \bar{C}_1 \operatorname{erf}\frac{x}{2\sqrt{(D_1 t)}} \quad (15)$$

and

$$C_2 = \bar{C}_2 - \frac{1}{m}\left(\frac{D_1}{D_2}\right)^{1/2}\bar{C}_1 \operatorname{erfc}\frac{|x|}{2\sqrt{(D_2 t)}}. \quad (16)$$

Conversely, when

$$m\left(\frac{D_2}{D_1}\right)^{1/2}\bar{C}_2 < \bar{C}_1$$

we have

$$C_1 = \bar{C}_1 - m\left(\frac{D_2}{D_1}\right)^{1/2}\bar{C}_2 \,.\, \operatorname{erfc}\frac{x}{2\sqrt{(D_1 t)}} \quad (17)$$

and

$$C_2 = \bar{C}_2 \operatorname{erf}\frac{|x|}{2\sqrt{(D_2 t)}}. \quad (18)$$

The instantaneous flux of component A is given by

$$N_i(t) \equiv D_1\left(\frac{\partial C_1}{\partial x}\right)_{x=0} = \bar{C}_1\left(\frac{D_1}{\pi t}\right) \quad (19a)$$

and

$$N_1(t) = m\,\bar{C}_2\sqrt{\left(\frac{D_1}{\pi t}\right)} \quad (19b)$$

for

$$C_1 < m\left(\frac{D_2}{D_1}\right)^{1/2}\bar{C}_2$$

and

$$C_1 > m\left(\frac{D_2}{D_1}\right)^{1/2}\bar{C}_2 \quad \text{respectively.}$$

Similar expressions can be derived for the flux of component B. The time averaged value of the flux can be evaluated from

$$\bar{N}(t) = \frac{1}{t_e}\int_0^{t_e} N(t)\,\mathrm{d}t. \quad (20)$$

It is seen that the effect of an instantaneous irreversible chemical reaction is to eliminate the "resistance to transfer" from one of the phases; thus the resultant expression for the flux is identical to that given by the Penetration Theory [4].

It is thought that the model presented for case (*a*) is a reasonable approximation for describing the rate at which silicon is removed from iron by oxidation in the Open Hearth steelmaking process.

(*b*) *Reversible reaction unaffected by the transport of products*

Consider an instantaneous reversible reaction occurring at the interface

$$A + B \rightleftharpoons Z$$

such that substances A and B are contained in phase 1, and phase 2 is made up of pure product Z.

The equilibrium relationship is given by:

$$\frac{C_1 C_2}{C_3} = K \quad (21)$$

which can be written for the case considered as

$$C_1 C_2 = K'. \quad (22a)$$

Equation (22a) gives the boundary condition relating concentrations at the interface, i.e.

$$\psi(C_i, C_j) = C_1 C_2 = K', \text{ at } x = 0. \quad (22b)$$

The boundary condition relating fluxes is given by:

$$D_1\frac{\partial C_1}{\partial x} = D_2\frac{\partial C_2}{\partial x}, \text{ at } x = 0. \quad (23)$$

Similarly to case (*a*) the constants A_i and A_j can be evaluated by applying the above boundary conditions to equations (9) and (10). After some arithmetic we obtain:

$$C_1 = \bar{C}_1 \operatorname{erf}\frac{x}{2\sqrt{(D_1 t)}} + \tfrac{1}{2}\left(\bar{C}_1 - \bar{C}_2\left(\frac{D_2}{D_1}\right)^{1/2} \pm \sqrt{\left\{\left[\bar{C}_1 - \bar{C}_2\left(\frac{D_2}{D_1}\right)^{1/2}\right]^2 + 4K'\left(\frac{D_2}{D_1}\right)^{1/2}\right\}}\right)\operatorname{erfc}\frac{x}{2\sqrt{(D_1 t)}} \quad (24)$$

and

$$C_2 = -\tfrac{1}{2}\left(\frac{D_1}{D_2}\right)^{1/2}\left(\bar{C}_1 - \bar{C}_2\left(\frac{D_2}{D_1}\right)^{1/2} \pm \sqrt{\left\{\left[\bar{C}_1 - \bar{C}_2\left(\frac{D_2}{D_1}\right)^{1/2}\right]^2 + 4K'\left(\frac{D_2}{D_1}\right)^{1/2}\right\}}\right) - \tfrac{1}{2}\left(\frac{D_1}{D_2}\right)^{1/2} \left(\bar{C}_1 + \bar{C}_2\left(\frac{D_2}{D_1}\right)^{1/2} \pm \sqrt{\left\{\left[\bar{C}_1 - \bar{C}_2\left(\frac{D_2}{D_1}\right)^{1/2}\right]^2 + 4K'\left(\frac{D_2}{D_1}\right)^{1/2}\right\}}\right)\operatorname{erf}\frac{x}{2\sqrt{(D_2 t)}} \quad (25)$$

It can be shown that these equations satisfy all the initial and boundary conditions. It is seen that when $K \to 0$ equations (24) and (25) reduce to (13) and (14), respectively. Similarly to case (*a*) the sign of the square root depends on the relative magnitudes of

$$\left[C_1 - C_2\left(\frac{D_2}{D_1}\right)^{1/2}\right]^2$$

and

$$4K'\left(\frac{D_2}{D_1}\right)^{1/2}.$$

It is noted that when $\bar{C}_1\bar{C}_2 = K'$, i.e. the bulk concentrations are in equilibrium, (24) and (25) simplify to

$$C_1 = \bar{C}_1 \quad (26)$$

and

$$C_2 = \bar{C}_2 \quad (27)$$

and there is no net transfer.

Expressions can be derived for the fluxes by differentiating (24) or (25) with respect to x, and substituting $x = 0$; i.e. for the flux of $A(C_1)$ we have:

$$N_1(t) = \tfrac{1}{2}\sqrt{\left(\frac{D_1}{\pi t}\right)}\left(\bar{C}_1 + \bar{C}_2\left(\frac{D_2}{D_1}\right)^{1/2} - \sqrt{\left\{\left[\bar{C}_1 - \bar{C}_2\left(\frac{D_2}{D_1}\right)^{1/2}\right]^2 + 4K\left(\frac{D_2}{D_1}\right)^{1/2}\right\}}\right). \quad (28)$$

This equation has practical application for calculating the overall rate of the C + O ⇌ CO reaction occurring at the surface of a CO bubble rising in the metal bath in some steelmaking processes [5].

(*c*) *General case of reversible reaction*

Consider an instantaneous reversible reaction taking place at the interface

$$A + B \rightleftharpoons Z$$

such that A is contained in phase 1, B and Z are contained in phase 2.

The equilibrium relationship, i.e. $\psi(C_i, C_j)$ is given by:

$$\frac{C_1 C_2}{C_3} = K \quad (29)$$

and the flux boundary conditions are as follows:

$$D_1\frac{\partial C_1}{\partial x} = -D_2\frac{\partial C_2}{\partial x} = D_3\frac{\partial C_3}{\partial x}, \text{ at } x = 0. \quad (30)$$

Substituting these into equations (9) and (10) we obtain:

$$C_1 = \bar{C}_1 - \tfrac{1}{2}\left(\frac{D_3}{D_1}\right)^{1/2} [\alpha \pm \sqrt{(\alpha^2 + 4\beta)}]\operatorname{erfc}\frac{x}{2\sqrt{(D_1 t)}} \quad (31)$$

$$C_2 = \bar{C}_2 - \tfrac{1}{2}\left(\frac{D_3}{D_1}\right)^{1/2} [\alpha \pm \sqrt{(\alpha^2 + 4\beta)}]\operatorname{erfc}\frac{|x|}{2\sqrt{(D_2 t)}} \quad (32)$$

$$C_3 = \bar{C}_3 + \tfrac{1}{2}[\alpha \pm \sqrt{(\alpha^2 + 4\beta)}]\operatorname{erfc}\frac{|x|}{2\sqrt{(D_3 t)}}. \quad (33)$$

Where

$$\alpha = \frac{(D_1 D_2)^{1/2}}{D_3}\left[K + \bar{C}_1\left(\frac{D_3}{D_2}\right)^{1/2} + \bar{C}_2\left(\frac{D_3}{D_1}\right)^{1/2}\right] \quad (34)$$

and

$$\beta = \frac{(D_1 D_2)^{1/2}}{D_3} (K\bar{C}_3 - \bar{C}_1 \bar{C}_2). \qquad (35)$$

It is seen that for $K\bar{C}_3 = \bar{C}_1\bar{C}_2$; $\beta = 0$ and therefore

$$\left.\begin{aligned} C_1 &= \bar{C}_1 \\ C_2 &= \bar{C}_2 \\ C_3 &= \bar{C}_3 \end{aligned}\right\} \text{ for all } t.$$

The fluxes of A, B and Z can be evaluated from equations (31–33). Thus for $Z(C_3)$ we have:

$$N_3(t) = \tfrac{1}{2}\left(\frac{D_3}{\pi t}\right) [\alpha - \sqrt{(\alpha^2 + 4\beta)}]. \qquad (36)$$

One practical application of this expression is the calculation of the overall rates of some slag metal interactions in the Open-Hearth steel-making process (e.g. the $FeO + Mn \rightleftharpoons MnO + Fe$).

DISCUSSION OF RESULTS

The paper considers the effect of instantaneous chemical reactions at the interface on diffusion in an infinite composite medium.

On the assumption of uniform initial values for the concentration, expressions are derived for concentrations and fluxes in case of second order reversible and irreversible reactions.

It is seen that the assumption of instantaneous reaction and restriction of the reaction to the phase boundary (this latter implies zero solubility of the reactants contained in one phase, in the other phase and vice versa) enables the results to be expressed in a comparatively simple closed analytical form. It is noted that the more general case of moving reaction zone [6] or finite reaction rate [7] results in rather more involved expressions even for essentially one phase systems.

The simplifying assumptions discussed may limit the applicability of the results, although in one class of problems, namely high temperature slag metal interactions, both these assumptions (i.e. instantaneous reaction and zero solubility of reactants in the "other phase") are thought to be realistic.

The results presented allow extension of the bubble-stirred interface model to systems with instantaneous surface reaction.

Possible practical applications are indicated in the text, a fuller discussion of their relevance to metallurgical systems will be given in a future publication [8].

REFERENCES

1. J. Szekely, Mathematical model for heat or mass transfer at the bubble-stirred interface of two immiscible liquids, *Int. J. Heat Mass Transfer*, **6**, 417 (1963).
2. J. Crank, *Mathematics of Diffusion*, p. 37. Oxford University Press (1957).
3. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, p. 87. Oxford University Press (1959).
4. R. Higbie, The rate of absorption of a pure gas into a still liquid during short periods of exposure, *Trans. Amer. Inst. Chem. Engng*. **31**, 365 (1935).
5. F. D. Richardson, Rates of slag-metal reactions and steelmaking processes, *Iron and Coal*, 1105 (1961).
6. T. K. Sherwood and R. L. Pigford, *Absorption and Extraction*, p. 320. McGraw-Hill, New York (1952).
7. Huang Chen-Jung and Hai-Kuo Chiang, General mathematical model for mass tranfer accompanied by chemical reaction, *A.I.Ch.E. J.* **9**, No. 2, 161 (1963).
8. J. Szekely, Notes on stirred interface transport as applied to some metallurgical processes. "Symposium on Chemical Engineering in Metallurgical Industries", p. 101. Edinburgh (September 1963).

Résumé—Cet article considère l'influence, sur la diffusion dans un milieu composite infini, des réactions chimiques instantanées à l'interface.

En faisant l'hypothèse de valeurs initiales uniformes on établit des expressions relatives aux champs de concentration et aux flux traversant l'interface, dans le cas de réactions du 2° ordre réversibles ou non. Les résultats permettent l'extension du modèle d'interface "turbulent" aux systèmes à réactions de surface instantanées et peuvent servir à interpréter certaines interactions métal-laitier dans les processus de fabrication de l'acier.

Zusammenfassung—Die Arbeit behandelt den Einfluss momentaner chemischer Reaktionen an der Trennfläche auf die Diffusion in einem unendlich ausgedehnten Gemisch.

Mit der Annahme einheitlicher Anfangswerte werden Ausdrücke abgeleitet für die "Felder" der Konzentration und für die Ströme durch die Trennfläche für reversible und irreversible Reaktionen zweiter Ordnung. Die Ergebnisse gestatten die Erweiterung des Modells mit blasengerührter Trennfläche auf Systeme mit momentaner Oberflächenreaktion und könnten zur Interpretation einiger Schlacke-Metall Reaktionen in Stahlgewinnungsprozessen dienen.

Аннотация—В статье рассматривается влияние химических реакций на поверхности раздела на процессы диффузии в бесконечной сложной среде.

С номощью допущения об однородности начальной концентрации выводятся выражения для «полей» концентраций и потоков в случае обратимых и необратимых реакций второго порядка. Полученные результаты дают возможность применить модель пузырькового кипения на поверхности раздела к системам, в которых имеет место поверхностная реакция, и использовать ее для обработки данных по взаимодействию металла со шлаком в металлургических процессах.