Heat and Mass Diffusion with Chemical Reaction: A Moving Boundary Analysis in a Particle

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Goodman's integral heat and mass balance method is applied to the problem of a moving boundary in a spherical particle. The moving boundary was fixed by a suitable transformation for ease in solution. The mean value theorem was used to treat the nonlinearities when they occurred. Relations for the heat and mass boundary positions are obtained for the most general conditions. These expressions reduce in their limiting cases to known results.

Problems involving a moving boundary are frequently encountered. Well-known examples are the melting-freezing problem in heat transfer and the intraparticle diffusion of heat and mass with chemical reactions. No closed form solutions are available for most moving boundary problems. The technique used in this analysis is that of the integral balance. This consists of integrating the partial differential equations over space and then substituting the boundary conditions in the integrated equations.

Many reaction-diffusion analyses consider the shrinking core model. Levenspiel (1962), and Yagi and Kunii (1962) have used the pseudo steady state postulate to obtain solutions to diffusion-reaction systems with a first-order reaction present. Bischoff (1963) and Theofanous and Lim (1971) have developed approximate solutions for first-order reaction cases with diffusion.

Goodman (1958) has applied the integral balance technique to solve moving boundary problems in heat conduction. Theofanous and Lim extended Goodman's analysis by integrating over space and time to reduce the system for heat conduction to an integro differential equation for the moving boundary. Dana (1964) has experimentally observed a moving diffusion layer in an ion exchange resin. Selim and Seagrave (1973) solved the moving boundary diffusion described by Dana by transforming the problem into a large set of integro differential equations and solving them numerically. More recently, Krishnamurthy and Shah (1979) used the Theofanous and Lim technique to solve the moving boundary diffusion of mass with a first-order irreversible chemical reaction.

ANALYSIS

The present model considers a spherical particle in which a chemical reaction occurs with heat effects. In general, there will be two moving boundaries, a mass moving boundary and a heat moving boundary.

If we consider a spherical particle surrounded by a fluid, reactant A in the fluid diffuses into the particle reaction to form B, while B then diffuses outward to the bulk fluid. A reaction zone is developed moving towards the center of the particle as time proceeds. Several assumptions are made on the system. The reactants are assumed to be uniformly distributed within the particle at a given radial position. No surface resistance is present, and all the physical properties are constant. The mass and energy balance equations are given in reduced dimensionless variables as

mass
$$\frac{\partial y}{\partial t} = \Delta y - r(y,z) \tag{1}$$

heat
$$(\mathrm{Le})\frac{\partial z}{\partial t} = \Delta z + B\, r(y,z) \tag{2}$$

The boundary conditions are given as

$$\text{at } x = 1 \quad y(x,t) = 1 \quad z(x,t) = 1$$

at
$$x = L_m \quad y(x,t) = 0$$

and
$$\frac{\partial y}{\partial x} = -\frac{B dL_m}{dt}$$

at
$$x = L_H \quad z\,(x,t) = \epsilon$$

and
$$\frac{\partial z}{\partial x} = -\frac{\mathrm{A\,d\,L_H}}{dt}$$

Often, $r(y,z)$ is a nonlinear function owing to the nature of the chemical reaction. Goodman's integral balance can be applied to this system, but difficulty is encountered in this analysis for the reaction term; however, the mean value theorem will be applied to this analysis to overcome this difficulty, Essoh (1979). In applying Goodman's integral balance, the spherical geometry is employing using the differential volume. The mass transfer model, Equation (1), is multipled by x^2dx and integrated between $x = 1$ and $x = L_m$, while the heat transfer equation is multiplied by the same expression and integrated between $x = 1$ and $x = L_H$. Thus one has

$$\int_{L_M}^{1} \frac{\partial y}{\partial t} x^2 dx = \int_{L_M}^{1} \Delta y\, x^2 dx - \int_{L_M}^{1} r(y,z)\, x^2 dx \tag{3}$$

and

$$(\mathrm{Le}) \int_{L_H}^{1} \frac{\partial z}{\partial t} x^2 dx = \int_{L_H}^{1} \Delta z\, x^2 dx + B \int_{L_H}^{1} r(y,z)\, x^2 dx \tag{4}$$

The domains of integration L_H and L_M are generally not the same. The integration can be performed on these equations to yield

$$\frac{d}{\mathrm{dt}}\left(\int_{L_M}^{1} x^2 y(x,t)\, dx\right) = \frac{\partial y}{\partial x}(1,t) + B\, L_M\, L_M{}^2 - \frac{\bar{r}}{3}(1 - L_M{}^3) \tag{5}$$

and

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$$Le \frac{d}{dt}\left(\int_{L_H}^{1} x^2 z(x,t)dx\right) + (Le)\,\epsilon\, L_H\, L_H^2 = \frac{\partial z}{\partial x}(1,t)$$

$$+ A\, L_H^1 L_H^2 + B\,\frac{\bar{r}}{3}(1 - L_H^3) \quad (6)$$

where

$$\bar{r} = \frac{r(y_2,z_2)}{r(y_1,z_3)} \qquad \frac{\int_{\epsilon}^{1} \int_0^1 r(y,z)\,dy\,dz}{(1-\epsilon)\,(1-0)}$$

Using an additional variable change, we get

$\eta = \frac{1}{3}(1 - x^3)$ a new independent variable

$\delta_m = \frac{1}{3}(1 - L_M^3)$ volume of mass diffusion zone

$\delta_H = \frac{1}{3}(1 - L_H^3)$ volume of heat diffusion zone

$$\xi = \eta/\delta_m$$

$$S = \eta/\delta_H$$

$$\Delta_m = \tfrac{1}{2}\cdot\delta_m^2$$

$$\Delta_h = \tfrac{1}{2}\cdot\delta_h^2$$

Equations (5) and (6) can be reduced further to

$$\frac{d}{dt}\left[\int_0^{\delta m} y(\eta,t)\,d\eta\right] = -\left.\frac{\partial y}{\partial \eta}\right|_{\eta=0} - B\,\delta_m' - \bar{r}\delta_m' \quad (7)$$

and

$$(Le)\,\frac{d}{dt}\int_0^{\delta H} z(\eta,t)\,d\eta = -\left.\frac{\partial z}{\partial \eta}\right|_{\eta=0}$$

$$+ (\epsilon\, Le - A)\,\delta_H' + B\,\bar{r}\,\delta_H \quad (8)$$

with the initial conditions

$$\delta_m(0) = 0$$

$$\delta_H(0) = 0$$

These integro differential equations can be changed to first-order equations by another variable change:

$$\xi = \eta/\delta_m \text{ and } S = \eta/\delta_H$$

By letting

$$M = \int_0^1 y(\xi,t)\,d\,\xi \quad (9)$$

and

$$H = \int_0^1 z(s,t)\,ds \quad (10)$$

one obtains the following first-order equation:

$$\Delta_m'\,(M + B) + 2(M' + \bar{r})\,\Delta_m = -\frac{\partial y}{\partial \xi}(0,t) \quad (11)$$

$$\Delta_H'\,(Le\,H + A - \epsilon Le) + 2(LeH' - B\bar{r})\,\Delta_H = \frac{\partial z}{\partial s}(0,t) \quad (12)$$

The boundary conditions applicable for this problem are

$$y(0,t) = 1, \qquad y(1,t) = 0$$
$$z(0,t) = 1, \qquad z(1,5) = \epsilon$$

For solution of Equations (11) and (12), an additional assumption is made. This involves assuming that the ratio of the first two coefficients of these equations are constant; that is, $(M' + \bar{r})/(M + B)$ and $(Le\,H' - B\bar{r})/(Le\,H + A - \epsilon Le)$ are constant. This assumption of constant ratios is substantiated later by the agreement seen between the present analysis and existing solutions. For making the analysis of the moving boundary, the term $\bar{r}$ must be developed. The terms y_2, z_2, y_1 and z_3 which are involved in the evaluation of $\bar{r}$ must be determined. These values cannot be determined a priori, but with the development of experimental data the appropriate values can be estimated. At the present time, data are lacking to set these reduced concentrations and temperatures at radial positions in the catalyst to represent the true mean for averaging. As an example, for analysis, the midpoint values are taken to evaluate the parameters over the boundary layers:

$$y_2 = \tfrac{1}{2}\left[y\Big|_{x=1} + y\Big|_{x=L_M}\right] = \tfrac{1}{2} \quad (13)$$

$$z_2 = \tfrac{1}{2}\left[z\Big|_{x=1} + z\Big|_{x=L_H}\right] = \tfrac{1}{2}(1+\epsilon) \quad (14)$$

$$y_1 = \tfrac{1}{2}\left[y_2 + y\Big|_{x=1}\right] = \frac{3}{4} \quad (15)$$

$$z_3 = \tfrac{1}{2}\left[z_2 + z\Big|_{x=L_H}\right] = 1+3\epsilon/4 \quad (16)$$

With the assumption that the ratios of coefficients of Equations (11) and (12) are constant, these equations can be easily solved because of their linear form. The nonhomogenous term in the equations can be evaluated by using concentration distribution $y(\xi)$ and temperature distributions $z(s)$ inside the particle. Goodman suggested functions of the form

$$y(\xi) = (1-\xi)^n(1-\xi^2)^m \quad (17)$$

$$z(s) = \epsilon + (1-\epsilon)\,(1-s)^p(1-s^2)^q \quad (18)$$

The validity of the above technique and assumptions will be tested on a number of know solutions for spherical geometries. Use of this technique for more complicated situations is conjectured.

PURE DIFFUSION EXAMPLE

For the case of pure mass diffusion with no chemical reaction $\bar{r} = 0$ and $\Delta_H(t) = 0$ simplifying the solution of Equation (11) is

$$\Delta_m(t) = -\left\{\frac{\partial y/\partial \xi\,(0)}{M + B}\right\} t \quad (19)$$

If we assume the concentration profile $y(\xi)$ to be

$$y(\xi) = (1-\xi)\,(1-\xi^2) \quad (20)$$

the constants evaluated using Equation (20) are

$$-(\partial y/\partial\ \xi\,(0) = 1 \text{ and } M = \int_0^1 y(\xi)\,d\xi = 5/12$$

With $B = C_r/C_s$

$$\Delta_m(t) = \left(\frac{12\,c_s}{5c_s + 12\,c_r}\right) t \quad (21)$$

which on expansion gives the mass transfer moving boundary as

$$R_m^3 = r_0^3 - 3r_0^2\left(\frac{24\,D_A c_s}{5c_s + 12\,c_r}\right)^{1/2} \sqrt{\theta} \quad (22)$$

This behavior of R_m with time has the classic square-root dependence.

DIFFUSION WITH A FIRST-ORDER REACTION EXAMPLE

For the case of diffusion with a first-order chemical reaction and no heat liberated, Equation (11) can be solved with $r(y,z) = \vartheta^2 y$, $\gamma = 0$ and $m = 0$ to yield

$$\Delta_m(t) = \frac{\left(\dfrac{-\dfrac{\partial y}{\partial \xi}(0)}{M+B}\right)}{2\bar{r}/(M+B)} \left({}_{1-e} - \frac{2\bar{r}}{M+B}\ t\right) \tag{23}$$

with

$$\bar{r} = k_0 r_0^2/2D$$

The term $\partial y/\partial \xi(0)$ can be found from the same assumed profile as shown in the previous example.

HEAT AND MASS DIFFUSION WITH AN N_{TH}-ORDER CHEMICAL REACTION

The general moving boundary solutions for constant coefficients for the case of an n_{th}-order chemical reaction are obtained from Equations (11) and (12) as

$$\Delta_m(t) = \frac{\left(\dfrac{-\dfrac{\partial y}{\partial \xi}(0)}{M+B}\right)}{2\bar{r}/(M+B)} \left({}_{1-e} - \frac{2\bar{r}}{M+B}\ t\right) \tag{24}$$

and

$$\Delta_H(t) = \left(\frac{-\dfrac{\partial z/\partial s(0)}{Le(H-\epsilon)+A}}{\dfrac{-2\beta\bar{r}}{Le\,(H-\epsilon)+A}}\right) \left({}_{1-e}\frac{2\beta\bar{r}}{Le\ (H-\epsilon)+A}\ t\right) \tag{25}$$

For an irreversible n_{th}-order reaction with a temperature dependency, one finds

$$r(y,z) = \vartheta^2 y^n z^m e^{\gamma(1-1/z)} \tag{26}$$

with m and n as integers. If $r(y_1, z_1)/r(y_2,z_2) \simeq 1$, one has

$$\bar{r} = \frac{\vartheta^2 e^{\gamma}}{(n+1)\,(1-\epsilon)} \left\{E_{m+2}(\gamma) - \epsilon^{m+1}E_{M+2}\left(\frac{\gamma}{\epsilon}\right)\right\} \tag{27}$$

with E_{m+2} as exponential integrals.

COMPARISON WITH EXISTING ANALYSES

For the case of pure diffusion inside a spherical particle, Selim and Seagrave have numerically addressed the problem. They obtained variations in the moving boundary with respect to dimensionless time for an elution constant of the order of 2.7. The value of the moving boundary (R_m/r_0) was extracted at various times from their graphical presentations. The values of (R_m/r_0) were then inserted in

$$\Delta_m = \frac{1}{18}\left[1 - \left(\frac{R_m}{r_0}\right)^3\right]^2 \tag{28}$$

to give Δ_m. The value of Δ_m was then plotted against time, and a straight line resulted in accordance with the result seen in Equation (19) which is also a linear representation of the mass transfer boundary layer with time over a dimensionless time variation of 0-5.0.

Krishnamurthy and Shah have also investigated the diffusion inside a particle, but with a first-order chemical reaction present. Again, their numerical results were presented in a graphical form. From these graphical representations, the moving boundary R_m/r_0 was found at various times. This again permitted Δ_m to be determined by Equation (28). The value of Δ_m was placed in a logarithmic form and plotted as suggested by Equation (24). When this analysis was performed again, a straight line was obtained pointing to the validity of Equation (23). The dimensionless time range investigated was from 0 → 0.16. For the examples considered, the Goodman integral technique using suitable averaging methods yielded good approximations to the numerical solutions. The potential exists in the proposed technique to give good approximate answers to more complex systems.

NOTATION

A = $\rho L^* D_A/\lambda T_s$
B = $C_r C_s$
C_p = heat capacity of solid
C_s = surface concentration
C_R = elution constant
c = concentration
D_A = diffusivity of species A
E = activation energy
k_0 = rate constant
L^* = latent heat of sublimation of the solid
Le = Lewis number, $\rho\, Cp\, D_A/\lambda$
L_H = R_H/r_0
L_M = R_M/r_0
m = rate term
n = constant in reaction
R = gas law constant
$R(c,T)$ = $k_0 c^n T^m e^{-E/RT}$
R_H = heat boundary radius
R_M = mass boundary radius
r = radius
r_0 = radius of the particle
$r(y,z)$ = reaction rate
T = temperature
T_0 = initial temperature
T_s = surface temperature
t = $D_A\Theta/r_0^2$
x = r/r_0
y = C/C_s
z = T/T_s

Greek Letters

β = $(-\Delta H)C_s D_A/\lambda T_s$
Δ = Laplacian operator
ΔH = heat of reaction
ϑ^2 = $k_0 C_s^{n-1} T_s^m r_0^2 e^{-}\gamma/D_A$
ϵ = T_0/T_s
Θ = time
ρ = density
γ = E/RT_s

Superscript

= differentiation with respect to time

LITERATURE CITED

Bischoff, K. B., "Accuracy of the Pseudo Steady State Approximation for Moving Boundary Diffusion Problems," *Chem. Eng. Sci.*, **18**, 711-713 (May, 1963).

Dana, P. R., "The Elution Kinetics of Hydrogen Ion in A Resin," Ph.D. thesis, Iowa State Univ., Ames (1969).

Essoh, D., "Analysis of the Heat and Mass Diffusion with Chemical Reaction in a Particle: Moving Boundary and Stability," M.S. thesis, Univ. of Pittsburgh, Pa (1979).

Goodman, T. R., "The Heat Balance Integral and Its Application to Problems Involving a Change of Phase," *Trans. ASME*, **80**, 335-342 (Feb., 1958).

Krishnamurthy, S. and Y. T. Shah, "An Approximate Solution to the Moving Boundary Problem with Two Simultaneous Reactions," *Chem. Eng. Sci*, (1979).

Levenspiel, O., *Chemical Reaction Engineering*, 2 ed., pp. 356-400, Wiley, New York (1962).

Selim, M. S., and R. C. Seagrave, "Solution of Moving Boundary Transport Problems in Finite Media by Integral Transforms. The Elution Kinetics of the Copper Amine Complex From a

Cation-Exchange Resin," *Ind Eng. Chem. Fundamentals*, **12**, No. 1 14-17 (Feb. 1973).

Theofanous, T. G., and H. C. Lim, "An Approximate Analytical Solution for Nonplanar Moving Boundary Problems," *Chem. Eng. Sci.*, **16**, 1297-1300 (1971).

Yagi, S., and D. Kunii, "Fluidized-Solid Reactors with Continuous Solids Feed - Residence Time of Particles in Fluidized Beds," *Chem. Eng. Sci.*, **16**, 364-391 (1962).

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Vapor-Liquid Equilibria Up to 40 000 KPa and 400°C: A New Static Method

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The present work was undertaken in order to obtain data for hydrogen-hydrocarbon systems at high pressures and temperatures. The cell materials and the measurement method were chosen with this objective. The method is especially suitable to study mixtures composed of at least one permanent gas and one high boiling liquid between 150° and 400°C and 5 000 and 40 000 KPa.

Both dynamic and static methods can be used at high temperatures and pressures. A static method seemed more appropriate for a not too expensive laboratory apparatus.

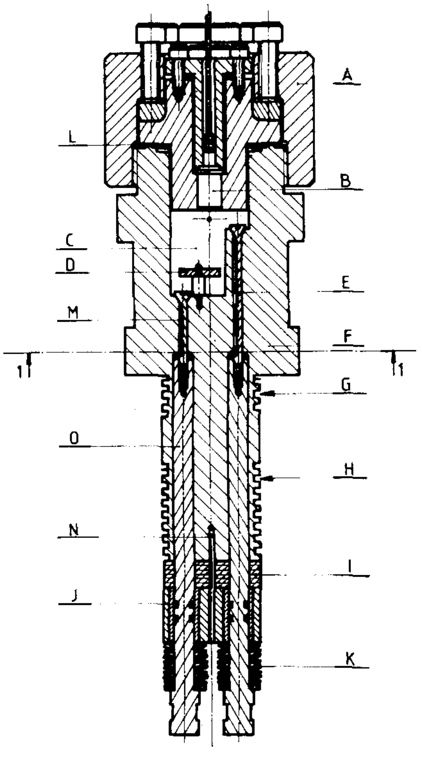

Figure 1a. Equilibrium cell: A cell cap, B pressure transducer, C equilibrium compartment, D magnetic stirrer, E valve, F cell body, G heating resistance place, H cooling coil place, I teflon thermal shield, J viton O-ring, K spring washers, L copper gasket, M channel, N thermocouple well, O valve pusher.

The existing sampling methods are not entirely satisfactory, and that is the reason which led us to devise a new sampling method.

The sampling procedure uses a microexpansion which is obtained through the rapid opening of a small aperture valve. The amount of withdrawn sample is small enough (about 1μl) not to modify equilibrium conditions in a 50 cm^3 cell. Such small samples can then be analyzed by means of gas-liquid chromatography.

EQUILIBRIUM CELL

The cell (Figure 1) is made of a special stainless steel which is amagnetic and hydrogen resistant.

The sampling system is located at the bottom of the cell body. Two holes were drilled through the cell bottom. The lower opening is used to sample the liquid phase, and the higher one samples the gas phase. These holes contain the stems of two valves, the seats of which are machined in the cell body material. The main difficulty is to achieve a reliable leakproof seal; we found that the best way is to deposit a smooth metal into the conical part of the valve. The samples flow through slits machined along the valve stems (Figure 1*b*) and encounter the chromatographic carrier gas at level 1.1 (Figure 1). Sampling is achieved thanks to rapid vertical percussions generated by a hammer activated by an electromagnet and transmitted to the valves by pushers, O (Figure 1). The valves are brought back on their seatings by very strong spring washers K (force ≃ 200 daN). Tightness around the pushers is achieved by means of viton O rings, J (Figure 1) which must be cooled not to be heat damaged. Heat transfer from top to bottom of the

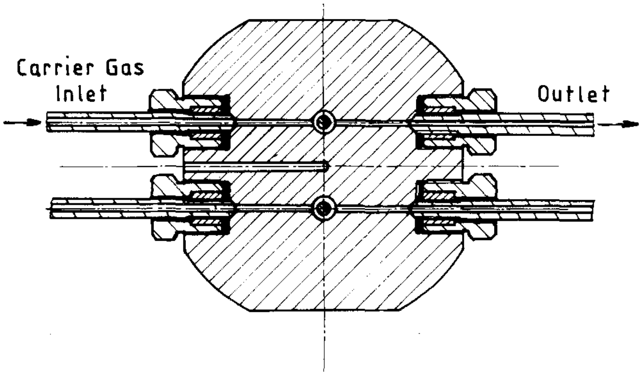

Figure 1*b*. Carrier gas circulation through the cell to sweep samples (cross section 1-1).

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