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Project Title: Thermally Induced Structural Changes in Coal Combustion

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Institution: California Institute of Technology

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I. Project Objectives

The project objectives are (1) to measure the effect of devolatilization temperature and time on the properties of the char and (2) characterize and quantify the effect of thermal annealing on char reactivity during char burnout under conditions of pulverized combustion.

II. Work Done During Reporting Period

1. Equipment Design and Construction

Work has continued during the reporting period on the modification of reactors I and II described in the previous quarterly report. This work has now been completed and the equipment is ready for experiments. Unfortunately, the graduate student who was scheduled to start the experiments decided to withdraw from the experimental program. Another student has been recruited who is going to begin experiments during the next few weeks.

2. Mathematical Modeling

Theoretical work on the effect of particle shape or combustion has continued. This work follows the following plan:

- a. mathematical analysis, numerical algorithm development and coding for the external mass transfer problem, neglecting the Stefan flow term (linear problem).
- b. same as (a) but with inclusion of the Stefan flow term (nonlinear problem).
- c. same as (b) but with inclusion of heat transfer and particle temperature as an unknown.

Phase (a) has been completed and a preliminary report on this work is attached as an appendix. The mathematical formulation of phase (b) has also been completed, but the numerical algorithm developed has run into convergence difficulties. Current work is focusing on resolving these convergence difficulties.

Attachment

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Appendix

External Mass Transfer to Nonspherical Char Particles under Isothermal Conditions

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ABSTRACT

The effect of particle shape on char burnout is investigated in the limit of shrinking core combustion. As a first step, the particle temperature is assumed known and combustion is assumed to proceed in the shrinking core regime and under conditions of negligible Stefan flow. The problem then reduces to calculating the oxygen concentration field around a non-spherical particle with the oxidation reaction taking place on the external surface. This problem has been addressed by an analytical technique and a numerical technique. An analytical technique known as "domain perturbation" was used to examine the change due to reaction in the shape of a slightly nonspherical, but axisymmetric, particle. It was found that the aspect ratio always increases with conversion, i.e., the particle becomes less spherical. A numerical technique, based on the "boundary integral" method was developed to handle the case of an axisymmetric particle with otherwise arbitrary shape. Numerical results are presented which again show the aspect ratio to increase with conversion.

1. Introduction.

Char particles generated by the rapid devolatilization of pulverized coal, vary widely in size and shape. The particle shape of char from softening coals(e.g., high volatile bituminous) is generally rounded and nearly spherical. Particles from non-softening coals(e.g.,lignites) are more irregular and deviate more from the spherical shape. In a recent experimental study we measured average aspect raatios of 1.15 and 1.35 for a softening bituminous coal and a lignite respectively.

All current models of particle combustion assume spherical shape to avoid the very considerable complications entailed by the fully three dimensional problem posed by nonspherical particles. Although this approximation is highly desirable, it is important to analyze the error introduced by the assumption of spherical shape on paarticle ignition, burnout time and maximum temperature. It should be noted in this connection that the particle shape changes during reaction and even a slightly nonspherical particle may become less and less spherical with increasing conversion, at least in the limit of shrinking core combustion.

With nonspherical particles, the temperature and oxygen concentration are fuctions of three spatial variables (rather than one as in the spherical case), and must be described by systems of partial differential equations. The problem is complicated further by the strong nonlinear temperature dependence of the reaction rate and the evolving porosity and particle size and shape. To make progress we have taken a step-by-step approach, The first step is to develop the analytical and numerical machinery required for solving the linear mass transfer problem, assuming isothermal conditions, negligible Stefan flow (which induces nonlinearity) and shrinking core combustion. This first problem is addressed in this report for

axially symmetric particles.

The two techniques used here to investigate how the shape of a nonspherical particle varies with conversion are 1) the method of domain perturbation and 2) the boundary integral method(BIM). When Stefan flow is included, we end up with the Laplace equation and a nonlinear boundary condition by adopting a new variable. We solve this problem by using the method of domain perturbation under the condition of diffusion control. The method of domain perturbation can only be applied to particles whose shapes are slightly different from spherical. The BIM has the advantage that the number of unknowns to be calculated can be greatly reduced by confining the numerical computations to the boundaries only. Then, we show the results for prolate spheroids with moderate aspect ratio. Both of these two methods are frequently used to study various free boundary problems related to fluid mechanics[3,4].

2. Mathematical Formulation.

Consider a solid or liquid particle which is composed of species P that reacts with some gas species,A. As this reaction continues, species P moves from the particle to the surroundings as gas product, B and species, A diffuses onto the particle surface.

Since this process or similar ones are common in chemical engineering processes, a great deal of research has already been done on those processes. It is very easy to obtain the solution to this problem if the particle has the shape of sphere. Therefore, in this paper we want to find the effect of a small perturbation of the particle surface

from a sphere with the method of domain perturbation. Then we'll solve the same problem for moderate aspect ratios by using BIM.

We make the mathematical formulation in this chapter with the two types of diffusion model. One is the linear diffusion (no Stefan flow) and the other is the diffusion including Stefan flow. The former is the asymptotic result of the latter either in case of the equimolar counterdiffusion or in case of a small amount of the species, A.

2.1. Linear diffusion.

2.1.1. Derivation of the governing equation and boundary conditions.

To make the problem simpler, the following assumptions are needed.

1. The surroundings consist mainly of an inert material.
2. The whole system is isothermal.
3. Reaction occurs only on the solid surface.
4. Reaction is first order and is proportional to the concentration of species A.
5. All the transport coefficients and physical properties are constant.
6. Since the particle shrinks very slowly, the concentration profile of species A is in quasi-steady state.

The first assumption is required so that species A experience nearly molecular diffusion only. Even though the quasi-steady state assumption is not strictly valid in a semi-infinite medium, it leads fortuitously to the correct result[5].

Under the above assumptions, we can derive the following governing equation and boundary conditions.

$$\nabla_{\vec{x}}^2 c_A = 0 \quad \text{outside the particle.} \quad (2.1)$$

$$-D_A \nabla_{\vec{x}} c_A \cdot \tilde{\mathbf{n}} = k c_A \quad \text{on the particle surface.} \quad (2.2)$$

$$c_A \rightarrow c_{Ab} \quad \text{as } |\mathbf{x}| \rightarrow \infty. \quad (2.3)$$

$$\frac{1}{|\nabla \tilde{F}|} \frac{\partial \tilde{F}}{\partial t} - \mathbf{v}_s \cdot \tilde{\mathbf{n}} = 0 \quad \text{on the particle surface.} \quad (2.4)$$

$$\tilde{F} \equiv \tilde{\rho} - \tilde{R}(\theta, t). \quad (2.5)$$

Here $\tilde{\mathbf{n}}$ is the unit normal vector on the surface whose direction is outward from the domain and $\mathbf{v}_s$ is the surface velocity. In this case the domain is the surroundings outside the particle.

Since we want to study the effect of a small perturbation from a perfect sphere in the first place, it is most convenient to use spherical coordinates. Then, eq.'s (2.1)-(2.5) are expressed as

$$\frac{1}{\tilde{\rho}^2} \frac{\partial}{\partial \tilde{\rho}} \left(\tilde{\rho}^2 \frac{\partial c_A}{\partial \tilde{\rho}} \right) + \frac{1}{\tilde{\rho}^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial c_A}{\partial \theta} \right) = 0 \quad \text{outside the particle,} \quad (2.6)$$

$$D_A \left(\alpha \frac{\partial c_A}{\partial \tilde{\rho}} - \frac{\beta}{\tilde{\rho}} \frac{\partial c_A}{\partial \theta} \right) = k c_A \quad \text{at } \tilde{\rho} = \tilde{R}(\theta, t), \quad (2.7)$$

$$c_A \rightarrow c_{Ab} \quad \text{as } \tilde{\rho} \rightarrow \infty, \quad (2.8)$$

$$-\frac{\partial \tilde{R}}{\partial t} = \frac{k}{b_1 \rho_s \alpha} c_A \quad \text{at } \tilde{\rho} = \tilde{R}(\theta, t). \quad (2.9)$$

Here, $\tilde{\mathbf{n}}$ is defined as

$$\tilde{\mathbf{n}} = -\alpha \mathbf{i}_{\tilde{\rho}} + \beta \mathbf{i}_{\theta}, \quad (2.10)$$

where

$$\alpha = \frac{1}{\sqrt{1 + \left(\frac{1}{\tilde{R}} \frac{\partial \tilde{R}}{\partial \theta} \right)^2}} \quad \text{and} \quad \beta = \frac{\frac{1}{\tilde{R}} \frac{\partial \tilde{R}}{\partial \theta}}{\sqrt{1 + \left(\frac{1}{\tilde{R}} \frac{\partial \tilde{R}}{\partial \theta} \right)^2}}. \quad (2.11)$$

Refer to Figure 1. Eq.'s (2.4) and (2.5) are derived in Appendix I.

We need to use dimensionless variables to simplify the appearance of the governing equation and the boundary conditions. By using

$$\mathbf{x} = \frac{\tilde{\mathbf{x}}}{\tilde{R}_s(t)}, u_A = \frac{c_A}{c_{Ab}} = \frac{y_A}{y_{Ab}}, R(\theta, t) = \frac{\tilde{R}(\theta, t)}{\tilde{R}_s(t)} \quad (2.12)$$

and

$$Q(\tilde{R}_s(t)) = \frac{k\tilde{R}_s(t)}{D_A}, \tau = \frac{k^2 c_{Ab}}{b_1 \rho_s D_A} t, \quad (2.13)$$

where $\tilde{R}_s(t)$ is the radius of the fictitious sphere which has the same volume as that of the particle. Then, we get the following dimensionless governing equation and boundary conditions.

$$\nabla_x^2 u_A = 0. \quad (2.14)$$

$$R^2 \frac{\partial u_A}{\partial \rho} - \frac{\partial R}{\partial \theta} \frac{\partial u_A}{\partial \theta} = QR^2 \sqrt{1 + \left(\frac{1}{R} \frac{\partial R}{\partial \theta} \right)^2} u_A \quad \text{at } \rho = R(\theta, \tau). \quad (2.15)$$

$$u_A \rightarrow 1 \quad \text{as } \rho \rightarrow \infty. \quad (2.16)$$

$$- \left(\frac{dQ(\tau)}{d\tau} R + Q(\tau) \frac{\partial R}{\partial \tau} \right) = \sqrt{1 + \left(\frac{1}{R} \frac{\partial R}{\partial \theta} \right)^2} u_A \quad \text{at } \rho = R(\theta, \tau). \quad (2.17)$$

2.1.2. Conditions on $R(\theta, t)$.

From the definition of $\tilde{R}_s(t)$, $R(\theta, \tau)$ must satisfy the following volume conservation condition.

$$\int_{-1}^1 R^3(\theta, \tau) d\eta = 2, \quad (2.18)$$

where

$$\eta = \cos \theta. \quad (2.19)$$

Furthermore, $R(\theta, \tau)$ should be defined so that the center of mass of the particle remains at the origin. This condition is expressed as

$$\int_{-1}^1 R^4(\theta, \tau) \eta d\eta = 0. \quad (2.20)$$

2.1.3. Rate of change of aspect ratio.

The aspect ratio is defined as

$$A_p = \frac{R(0)}{R(\frac{\pi}{2})}. \quad (2.21)$$

So, the rate of change of aspect ratio is expressed as

$$\frac{dA_p}{d\tau} = \frac{1}{R^2(\frac{\pi}{2})} \left[\frac{\partial R}{\partial \tau}(0)R(\frac{\pi}{2}) - R(0)\frac{\partial R}{\partial \tau}(\frac{\pi}{2}) \right]. \quad (2.22)$$

By the way, since eq.(2.17) may be changed to

$$\frac{\partial R}{\partial \tau} = -\frac{1}{Q(\tau)} \frac{dQ(\tau)}{d\tau} R - \frac{1}{Q(\tau)} \sqrt{1 + \left(\frac{1}{R} \frac{\partial R}{\partial \theta} \right)^2} u. \quad (2.23)$$

and $\frac{\partial R}{\partial \theta} = 0$ at $\theta = 0, \frac{\pi}{2}$, substitution of eq.(2.23) in eq.(2.22) gives

$$\frac{dA_p}{d\tau} = \frac{1}{R^2(\frac{\pi}{2})Q(\tau)} \left[R(0)u(\frac{\pi}{2}) - R(\frac{\pi}{2})u(0) \right]. \quad (2.24)$$

If we divide both sides of eq.(2.24) by $R(0) - R(\frac{\pi}{2})$, we get

$$\frac{d \ln(A_p - 1)}{d\tau} R(\frac{\pi}{2})Q(\tau) = \frac{A_p u(\frac{\pi}{2}) - u(0)}{A_p - 1}. \quad (2.25)$$

If the particle is a prolate spheroid, $R(\frac{\pi}{2}) = A_p^{-1/3}$ and

$$\frac{dA_p}{d\tau} = \frac{1}{Q(\tau)} \frac{A_p u(\frac{\pi}{2}) - u(0)}{A_p - 1} A_p^{1/3} (A_p - 1). \quad (2.26)$$

Note that we can obtain the rate of change of aspect ratio from eq.(2.25) or eq.(2.26) if we calculate the surface concentrations. In order to do this calculation, we use either the method of domain perturbation or the boundary integral method. These methods are explained in the following Ch.3 and Ch.5.

Let's call the right hand side of eq.(2.25) RHS from now on. As Q approaches to 0, u also goes to 1 all over the surface of particle. So, the RHS goes to 1 as Q

goes to 0. Conversely, since u becomes very small as Q gets very large within the range where the assumption of quasi-steady state is valid, the RHS should also get very small. Now we need to consider what happens with a finite amount of Q .

2.2. Case of binary diffusion.

In this case we are considering both the molecular diffusion and the convection. Since it is assumed that the inert material does not diffuse, we only have to consider the binary counterdiffusion of A and B.

We start with the following general governing equation and boundary conditions.

$$\nabla \cdot \mathbf{N}_A = 0. \quad (2.27)$$

$$\mathbf{N}_A \cdot \tilde{\mathbf{n}} = kc_A \quad \text{on the particle surface.} \quad (2.28)$$

$$c_A \rightarrow c_{Ab} \quad \text{as } |\tilde{\mathbf{x}}| \rightarrow \infty. \quad (2.29)$$

$$\frac{1}{|\nabla \tilde{F}|} \frac{\partial \tilde{F}}{\partial t} - \mathbf{v}_s \cdot \tilde{\mathbf{n}} = 0 \quad \text{on the particle surface.} \quad (2.30)$$

$$\tilde{F} \equiv \tilde{\rho} - \tilde{R}(\theta, t). \quad (2.31)$$

The following *ad hoc* assumption is necessary for mathematical formulation.

$$\mathbf{N}_B + b_2 \mathbf{N}_A = 0, \quad (2.32)$$

which is perfectly true in case of a spherical particle, but which might be controversial generally. The mass flux is expressed as the sum of the convection and the molecular diffusion as follows.

$$\mathbf{N}_A = y_A(\mathbf{N}_A + \mathbf{N}_B) - cD_A \nabla y_A. \quad (2.33)$$

From eq.'s (2.32) and (2.33) we get

$$\mathbf{N}_A = -\frac{cD_A \nabla y_A}{1 + (b_2 - 1)y_A}. \quad (2.34)$$

If we use a new variable defined as

$$\psi \equiv \ln(y_A + \frac{1}{b_2 - 1}) \quad (2.35)$$

in case of $b_2 > 1$, we get again Laplace equation for the governing equation as follows.

$$\nabla^2 \psi = 0. \quad (2.36)$$

$$-\nabla \psi \cdot \tilde{\mathbf{n}} = \frac{k(b_2 - 1)}{D_A} \left(e^\psi - \frac{1}{b_2 - 1} \right) \quad \text{on the particle surface.} \quad (2.37)$$

If we use the same dimensionless variables as in the section 2.1 except ψ , then we get the following dimensionless forms of governing equations and boundary conditions.

$$\nabla^2 \psi = 0. \quad (2.38)$$

$$-\nabla \psi \cdot \mathbf{n} = Q(b_2 - 1) \left(e^\psi - \frac{1}{b_2 - 1} \right) \quad \text{at } \rho = R. \quad (2.39)$$

$$\psi \rightarrow \psi_b \quad \text{as } |\mathbf{x}| \rightarrow \infty. \quad (2.40)$$

$$-y_{Ab} \left(\frac{dQ}{d\tau} R + Q \frac{\partial R}{\partial \tau} \right) = \sqrt{1 + \left(\frac{1}{R} \frac{\partial R}{\partial \theta} \right)^2} \left(e^\psi - \frac{1}{b_2 - 1} \right) \quad \text{at } \rho = R \quad (2.41)$$

In case of $0 < b_2 < 1$, we need to define

$$\psi = \ln \left(\frac{1}{1 - b_2} - y_A \right). \quad (2.42)$$

Then we get

$$\nabla^2 \psi = 0. \quad (2.43)$$

$$-\nabla \psi \cdot \mathbf{n} = Q(1 - b_2) \left(e^\psi - \frac{1}{1 - b_2} \right) \quad \text{at } \rho = R. \quad (2.44)$$

$$\psi \rightarrow \psi_b \quad \text{as } |\mathbf{x}| \rightarrow \infty. \quad (2.45)$$

$$-y_{Ab} \left(\frac{dQ}{d\tau} R + Q \frac{\partial R}{\partial \tau} \right) = \sqrt{1 + \left(\frac{1}{R} \frac{\partial R}{\partial \theta} \right)^2} \left(\frac{1}{1 - b_2} - e^\psi \right) \quad \text{at } \rho = R \quad (2.46)$$

3. Domain Perturbation in case of molecular diffusion.

Since we are restricting our problem to the case in which the shape of the particle is only slightly different from spherical, $R(\theta, \tau)$ and $u(\rho, \theta, \tau)$ can be expressed as

$$R(\theta, \tau) = R_0(\theta, \tau) + \epsilon R_1(\theta, \tau) + \epsilon^2 R_2(\theta, \tau) + \dots \quad (3.1)$$

and

$$u(\rho, \theta, \tau) = u_0(\rho, \tau) + \epsilon u_1(\rho, \theta, \tau) + \epsilon^2 u_2(\rho, \theta, \tau) + \dots \quad (3.2)$$

By using this expression of $R(\theta, \tau)$ in eq.(2.18), we get the following conditions for $R_0(\theta, \tau)$, $R_1(\theta, \tau)$ and so on.

$$\int_{-1}^1 R_0^3 d\eta = 2. \quad (3.3)$$

$$\int_{-1}^1 R_0^2 R_1 d\eta = 0. \quad (3.4)$$

$$\int_{-1}^1 (R_0^2 R_2 + R_0 R_1^2) d\eta = 0. \quad (3.5)$$

$\vdots$

Similarly, we may use eq.(3.1) in eq.(2.20) to get

$$\int_{-1}^1 R_0^4 \eta d\eta = 0, \quad (3.6)$$

$$\int_{-1}^1 R_0^3 R_1 \eta d\eta = 0, \quad (3.7)$$

and

$$\int_{-1}^1 (4R_0^3 R_2 + 6R_0 R_1^3) \eta d\eta = 0. \quad (3.8)$$

$\vdots$

We may, without loss of any generality, let $R_0(\theta, 0)$ be a function which is independent of θ . Then, by inspection of the governing equation and B.C.'s, we can see that $R_0(\theta, \tau)$ should not be a function of θ . Thus it follows from eq.(3.3) that

$$R_0(\theta, \tau) \equiv 1 \quad (3.9)$$

and eq.'s (3.4)-(3.8) are reduced to

$$\int_{-1}^1 R_1 d\eta = 0, \quad (3.10)$$

$$\int_{-1}^1 (R_2 + R_1^2) d\eta = 0, \quad (3.11)$$

$$\int_{-1}^1 R_1 \eta d\eta = 0, \quad (3.12)$$

and

$$\int_{-1}^1 (4R_2 + 6R_1^3) \eta d\eta = 0. \quad (3.13)$$

First of all, our initial shape of the particle should satisfy the above conditions. We can choose $R_1(\theta, 0)$ and $R_2(\theta, 0)$ so that the resultant mathematical equations are reduced to the simplest form. One set of functions is

$$R_1(\theta, 0) = P_2(\eta) \quad (3.14)$$

and

$$R_2(\theta, 0) = -P_2^2(\eta). \quad (3.15)$$

Here, P_2 is the second Legendre function. So, let's assume the following initial shape of the particle.

$$R(\theta, 0) = 1 + \epsilon P_2 - \epsilon^2 P_2^2. \quad (3.16)$$

Since with this initial shape we have $O(\epsilon^3)$ -error in volume evaluation of the particle, we are allowed to find $R(\theta, \tau)$ and $u(\theta, \tau)$ up to $O(\epsilon^2)$. If we want to get the solution up to $O(\epsilon^n)$, we have to satisfy the volume condition of the initial shape up to $O(\epsilon^n)$.

Next, we have to change the boundary conditions from $\rho = R$ to $\rho = 1$ by using a Taylor series expansion around $\rho = 1$, and rearrange the terms to get ones of the same order together. Refer to Appendix II for detailed procedure for the derivation of the $O(\epsilon^n)$ problem.

3.1. $O(1)$ -problem.

We can derive the following $O(1)$ governing equation and boundary conditions.

$$\nabla^2 u_0 = 0. \quad (3.17)$$

$$\frac{\partial u_0}{\partial \rho} = Q u_0 \quad \text{at } \rho = 1. \quad (3.18)$$

$$u_0 \rightarrow 1 \quad \text{as } \rho \rightarrow \infty. \quad (3.19)$$

$$-\frac{dQ}{d\tau} = u_0 \quad \text{at } \rho = 1. \quad (3.20)$$

It turns out that the governing equation and boundary conditions for the $O(1)$ -problem are the same as those for a spherical shape. We can easily solve the above equations to get

$$u_0 = 1 - \left[\frac{Q}{Q+1} \right] \frac{1}{\rho} \quad (3.21)$$

and

$$Q(\tau) = -1 + \sqrt{(1 + Q_0)^2 - 2\tau}, \quad (3.22)$$

where Q_0 is the initial value of Q . Therefore we find

$$\frac{dQ(\tau)}{d\tau} = -\frac{1}{Q(\tau) + 1}. \quad (3.23)$$

It is natural that we should get the solution for the spherical shape as the leading order solution when the shape is only a small perturbation from a sphere.

3.2. $O(\epsilon)$ -problem.

The following first order governing equation and boundary conditions are derived.

$$\nabla^2 u_1 = 0. \quad (3.24)$$

$$u_1 \rightarrow 0 \quad \text{as } \rho \rightarrow \infty. \quad (3.25)$$

$$\frac{\partial u_1}{\partial \rho} - Qu_1 = \frac{Q(Q+2)}{Q+1} R_1 \quad \text{at } \rho = 1. \quad (3.26)$$

$$-\left(\frac{dQ}{d\tau} R_1 + Q \frac{\partial R_1}{\partial \tau}\right) = u_1 + \frac{\partial u_0}{\partial \rho} R_1 \quad \text{at } \rho = 1. \quad (3.27)$$

By using spherical harmonics and eq.(3.25), the first order solution is easily derived as follows.

$$u_1 = \sum_0^{\infty} \alpha_n(\tau) \rho^{-(n+1)} P_n(\eta) \quad (3.28)$$

where $P_n(\eta)$ is the n th Legendre function. Furthermore, R_1 is expressed as Legendre series in the form of

$$R_1 = \sum_0^{\infty} \beta_n(\tau) P_n(\eta), \quad (3.29)$$

By applying eq.'s (3.10) and (3.12) to eq.(3.29), R_1 should satisfy

$$\beta_0(\tau) = \beta_1(\tau) = 0. \quad (3.30)$$

From eq.(3.26) the following relationships are derived.

$$\alpha_0(\tau) = 0, \quad (3.31)$$

$$\alpha_1(\tau) = 0 \quad (3.32)$$

and

$$\alpha_n(\tau) = -\frac{Q(Q+2)}{(Q+1)(Q+n+1)}\beta_n(\tau) \text{ for } n \geq 3. \quad (3.33)$$

Then from eq.(3.27), we can derive

$$\frac{d\beta_n}{d\tau} = \gamma_n(\tau)\beta_n, \quad n = 0, 1, 2, \dots \quad (3.34)$$

where

$$\gamma_n(\tau) = -\frac{(n-2)Q - (n+1)}{Q(Q+1)(Q+n+1)}. \quad (3.35)$$

Therefore, we get

$$\beta_n(\tau) = \beta_n(0) \exp(\Gamma_n(\tau)), \quad (3.36)$$

where

$$\Gamma_n(\tau) = \int_0^\tau \gamma_n(s) ds. \quad (3.37)$$

In conclusion, R_1 and u_1 are expressed as

$$R_1 = \sum_2^\infty \beta_n(0) P_n(\eta) \exp(\Gamma_n(\tau)) \quad (3.38)$$

and

$$u_1 = -\sum_2^\infty \rho^{-(n+1)} \frac{Q(Q+2)}{(Q+1)(Q+n+1)} \beta_n(0) P_n(\eta) \exp(\Gamma_n(\tau)). \quad (3.39)$$

When the surface is convex and smooth,

$$\beta_2(\tau) \gg \beta_n(\tau). \quad (3.40)$$

Therefore,

$$R_1(\theta, 0) \simeq \beta_2(0) P_2(\eta) \quad (3.41)$$

and

$$u_1 \simeq \frac{Q(Q+2)}{(Q+1)(Q+3)} \beta_2(0) P_2(\eta) \exp(\Gamma_2(\tau)) \rho^{-3}. \quad (3.42)$$

3.3. Analysis.

Now we know that

$$R(\theta, \tau) \simeq 1 + \beta_2(\tau) P_2(\eta), \quad (3.43)$$

where

$$\beta_2(\tau) = \beta_2(0) \exp\left(\int_0^\tau \frac{3}{Q(Q+1)(Q+3)} ds\right). \quad (3.44)$$

Since $Q > 0$, $\beta_2(\tau)$ is monotonely increasing with respect to time. This means the shape of particle is deviating from the sphere further as time goes on.

Since

$$\begin{aligned} u|_{\rho=R} &= u|_{\rho=1} + \frac{\partial u}{\partial \rho}|_{\rho=1} (\epsilon R_1 + \dots) + \dots \\ &= u_0|_{\rho=1} + \epsilon (u_1|_{\rho=1} + \frac{\partial u_0}{\partial \rho}|_{\rho=1} R_1) + \dots, \end{aligned} \quad (3.45)$$

u is expressed on the surface as follows.

$$u|_{\rho=R} = \frac{1}{Q+1} + \epsilon \frac{Q}{(Q+1)(Q+3)} \beta_2(\tau) P_2 + O(\epsilon^2). \quad (3.46)$$

Eq.(3.45) may be expressed as

$$\frac{u|_{\rho=R} - u|_{sphere}}{R_{maz} - R_{min}} = \frac{2}{3} \frac{Q}{(Q+1)(Q+3)} + O(\epsilon), \quad (3.47)$$

where $u|_{sphere}$ is the surface concentration in case of a spherical particle. So, the longer the radius of a point on the surface is, the higher is the concentration. Therefore, the absolute rate of shrinking increases with the radius of the surface.

However, the object related to the change of shape is the relative rate of shrinking, which is expressed as $-\frac{1}{\bar{R}} \frac{\partial \bar{R}}{\partial \tau}$. That relative rate of shrinking is expressed as

$$\begin{aligned} -\frac{1}{\bar{R}} \frac{\partial \bar{R}}{\partial \tau} \Big|_{\tau=0} &\propto \frac{u|_{\rho=R}}{R} \\ &\propto \frac{1}{Q+1} \left(1 - \epsilon \frac{3}{Q+3} \beta_2 P_2 \right) + O(\epsilon^2), \end{aligned} \quad (3.48)$$

Therefore, the relative shrinking rate is decreasing with the radius.

We can derive the aspect ratio as

$$A_p = 1 + \frac{3}{2} \epsilon \beta_2(\tau) \quad (3.49)$$

and RHS as

$$RHS = \frac{3}{(Q+1)(Q+3)} + O(\epsilon), \quad (3.50)$$

The above two equations show the same asymptotic behavior as was found in 2.1.3. Eq.'s (3.47) and (3.50) are shown as solid lines in Figure 3 and Figure 4 .

4. Domain Perturbation in case of binary diffusion.

We can just follow the method used in Ch.3. Then, $R(\theta, \tau)$ and $\psi(\rho, \theta, \tau)$ are expanded as

$$R(\theta, \tau) = 1 + \epsilon R_1(\theta, \tau) + \epsilon^2 R_2(\theta, \tau) + \dots \quad (4.1)$$

and

$$\psi(\rho, \theta, \tau) = \psi_0(\rho, \tau) + \epsilon \psi_1(\rho, \theta, \tau) + \epsilon^2 \psi_2(\rho, \theta, \tau) + \dots \quad (4.2)$$

Here we solve the problem in case of $b_2 > 1$. The same method could be applied in case of $0 < b_2 < 1$ to solve eq.'s (2.42)-(2.46), but it turns out that the same final results are obtained.

4.1. $O(1)$ -problem.

We can derive the following $O(1)$ governing equation and boundary conditions as follows.

$$\nabla^2 \psi_0 = 0. \quad (4.3)$$

$$\frac{d\psi_0}{d\rho} = Q(b_2 - 1) \left(e^{\psi_0} - \frac{1}{b_2 - 1} \right) \quad \text{at } \rho = 1. \quad (4.4)$$

$$\psi_0 \rightarrow \psi_b \quad \text{as } \rho \rightarrow \infty. \quad (4.5)$$

$$-y_{Ab} \frac{dQ}{d\tau} = e^{\psi_0} - \frac{1}{b_2 - 1} \quad \text{at } \rho = 1. \quad (4.6)$$

From eq.'s (4.3) and (4.5), we get

$$\psi_0 = \psi_b - \frac{c_1}{\rho}, \quad (4.7)$$

where the integration constant c_1 is determined by eq.(4.4). By substituting eq.(4.7) in eq.(4.4), we get

$$c_1 = \ln[1 + (b_2 - 1)y_{Ab}] - \ln\left(1 + \frac{c_1}{Q}\right). \quad (4.8)$$

When the diffusion controls ($Q \gg 1$), c_1 is approximately

$$c_1 \simeq \frac{Q}{1 + Q} \ln[1 + (b_2 - 1)y_{Ab}] + \frac{1}{2} \left(\frac{\ln[1 + (b_2 - 1)y_{Ab}]}{1 + Q} \right)^2 + O(Q^{-3}). \quad (4.9)$$

Therefore since at $\rho = 1$

$$\psi_0 = \psi_b - c_1, \quad (4.10)$$

we have

$$\psi_0 \simeq -\ln(b_2 - 1) + \frac{\ln[1 + (b_2 - 1)y_{Ab}]}{1 + Q} - \frac{1}{2} \left(\frac{\ln[1 + (b_2 - 1)y_{Ab}]}{1 + Q} \right)^2 + O(Q^{-3}) \quad (4.11)$$

and

$$e^{\psi_0} \simeq \frac{1}{b_2 - 1} \left(1 + \frac{\ln[1 + (b_2 - 1)y_{Ab}]}{1 + Q} \right) + O(Q^{-3}) \quad (4.12)$$

at $\rho = 1$. Substitution of eq.(4.12) in eq.(4.6) gives us

$$Q(\tau) = -1 + \sqrt{(1 + Q_0)^2 - 2 \frac{\ln[1 + (b_2 - 1)y_{Ab}]}{(b_2 - 1)y_{Ab}} \tau}. \quad (4.13)$$

4.2. $O(\epsilon)$ -problem.

The following first order governing equation and boundary conditions are derived.

$$\nabla^2 \psi_1 = 0. \quad (4.14)$$

$$\psi_1 \rightarrow 0 \quad \text{as } \rho \rightarrow \infty. \quad (4.15)$$

$$\frac{\partial \psi_1}{\partial \rho} = Q(b_2 - 1) \left[2R_1 \left(e^{\psi_0} - \frac{1}{b_2 - 1} \right) + e^{\psi_0} \left(\psi_1 + \frac{d\psi_0}{d\rho} R_1 \right) \right] \quad \text{at } \rho = 1. \quad (4.16)$$

$$\left(e^{\psi_0} - \frac{1}{b_2 - 1} \right) - y_{Ab} Q \frac{\partial R_1}{\partial \tau} = e^{\psi_0} \left(\psi_1 + \frac{d\psi_0}{d\rho} R_1 \right) \quad \text{at } \rho = 1. \quad (4.17)$$

By using spherical harmonics and eq.(4.15), the first order solution is easily derived as follows.

$$\psi_1 = \sum_0^{\infty} \alpha_n(\tau) \rho^{-(n+1)} P_n(\eta) \quad (4.18)$$

where $P_n(\eta)$ is the n th Legendre function. Furthermore, R_1 is expressed as Legendre series in the form of

$$R_1 = \sum_0^{\infty} \beta_n(\tau) P_n(\eta), \quad (4.19)$$

By applying eq.'s (3.10) and (3.12) to eq.(4.19), R_1 should satisfy

$$\beta_0(\tau) = \beta_1(\tau) = 0. \quad (4.20)$$

From eq.(4.16) the following relationships are derived.

$$\alpha_0(\tau) = 0, \quad (4.21)$$

$$\alpha_1(\tau) = 0 \quad (4.22)$$

and

$$\alpha_n(\tau) = -Q(b_2 - 1) \frac{2(e^{\psi_0} - \frac{1}{b_2 - 1}) + c_1 e^{\psi_0}}{n + 1 + Q(b_2 - 1)e^{\psi_0}} \beta_n \quad \text{for } n \geq 2. \quad (4.23)$$

Then from eq.(4.17), we can derive

$$\frac{d\beta_2}{d\tau} = \gamma_2(\tau)\beta_2, \quad (4.24)$$

where

$$\gamma_2(\tau) = \frac{3 \frac{\ln[1+(b_2-1)y_{Ab}]}{(b_2-1)y_{Ab}}}{Q(1+Q) \left(3 + Q + \frac{Q}{1+Q} \ln[1+(b_2-1)y_{Ab}] \right)} + O(O^{-4}) + O(\epsilon). \quad (4.25)$$

Therefore, we get

$$\beta_2(\tau) = \beta_2(0) \exp(\Gamma_2(\tau)), \quad (4.26)$$

where

$$\Gamma_2(\tau) = \int_0^\tau \gamma_2(s) ds. \quad (4.27)$$

When the surface is convex and smooth,

$$\beta_2(\tau) \gg \beta_n(\tau). \quad (4.28)$$

Therefore,

$$R_1(\theta, 0) \simeq \beta_2(0) P_2(\eta) \quad (4.29)$$

and

$$\psi_1 \simeq -Q(b_2 - 1) \frac{2(e^{\psi_0} - \frac{1}{b_2 - 1}) + c_1 e^{\psi_0}}{3 + Q(b_2 - 1)e^{\psi_0}} \beta_2(0) P_2(\eta) \exp(-\Gamma_2(\tau)) \rho^{-3}. \quad (4.30)$$

4.3. Analysis.

Now we know that

$$R(\theta, \tau) \simeq 1 + \epsilon \beta_2(\tau) P_2(\eta), \quad (4.31)$$

where

$$\beta_2(\tau) = \beta_2(0) \exp \left(\int_0^\tau \frac{3 \frac{\ln[1+(b_2-1)y_{Ab}]}{(b_2-1)y_{Ab}}}{Q(1+Q) \left(3 + Q + \frac{Q}{1+Q} \ln[1+(b_2-1)y_{Ab}] \right)} ds \right). \quad (4.32)$$

Since $Q > 0$, $\beta_2(\tau)$ is monotonely increasing with respect to time. This means the shape of particle is deviating from the sphere further as time goes on.

Since

$$\begin{aligned} y_A|_{\rho=R} &= e^{\psi|_{\rho=R}} - \frac{1}{b_2 - 1} \\ &= \exp(\psi_0|_{\rho=1}) \left[1 + \epsilon \left(\psi_1|_{\rho=1} + \frac{\partial \psi_0}{\partial \rho}|_{\rho=1} R_1 \right) + O(\epsilon^2) \right] - \frac{1}{b_2 - 1}, \end{aligned} \quad (4.33)$$

u_A is expressed on the surface as follows.

$$\begin{aligned} u_A|_{\rho=R} &= \frac{\ln[1+(b_2-1)y_{Ab}]}{(b_2-1)y_{Ab}} \frac{1}{1+Q} \times \\ &\left(1 + \epsilon \frac{Q + \frac{Q}{1+Q} \ln[1+(b_2-1)y_{Ab}]}{3 + Q + \frac{Q}{1+Q} \ln[1+(b_2-1)y_{Ab}]} \beta_2(\tau) P_2 \right) + O(Q^{-3}) + O(\epsilon Q^{-3}) + O(\epsilon^2). \end{aligned} \quad (4.34)$$

Eq.(4.33) may be expressed as

$$\begin{aligned} \frac{u_A|_{\rho=R} - u_A|_{sphere}}{R_{max} - R_{min}} &= \frac{2 \ln[1+(b_2-1)y_{Ab}]}{3 (b_2-1)y_{Ab}} \times \\ &\frac{1}{1+Q} \frac{Q + \frac{Q}{1+Q} \ln[1+(b_2-1)y_{Ab}]}{3 + Q + \frac{Q}{1+Q} \ln[1+(b_2-1)y_{Ab}]} + O(Q^{-2}) + O(\epsilon), \end{aligned} \quad (4.35)$$

where $u|_{sphere}$ is the surface concentration in case of a spherical particle. So, the longer the radius of a point on the surface is, the higher is the concentration.

Therefore, the absolute rate of shrinking increases with the radius of the surface. However, the object related to the change of shape is the relative rate of shrinking, which is expressed as $-\frac{1}{\tilde{R}} \frac{\partial \tilde{R}}{\partial \tau}$. That relative rate of shrinking is expressed as

$$-\frac{1}{\tilde{R}} \frac{\partial \tilde{R}}{\partial \tau} \Big|_{\tau=0} \propto \frac{u_A|_{\rho=R}}{R}$$

$$\propto \frac{\ln[1 + (b_2 - 1)y_{Ab}]}{(b_2 - 1)y_{Ab}(1 + Q)} \left[1 - \epsilon \frac{3}{Q + 3 + \frac{Q}{1+Q} \ln[1 + (b_2 - 1)y_{Ab}]} \beta_2 P_2 \right]$$

$$+ O(Q^{-3}) + O(\epsilon Q^{-3}) + O(\epsilon^2), \quad (4.36)$$

Therefore, the relative shrinking rate is decreasing with the radius.

We can derive the aspect ratio as

$$A_p = 1 + \frac{3}{2} \epsilon \beta_2(\tau) \quad (4.37)$$

and RHS as

$$RHS = \frac{3 \frac{\ln[1 + (b_2 - 1)y_{Ab}]}{(b_2 - 1)y_{Ab}}}{(1 + Q) \left(3 + Q + \frac{Q}{1+Q} \ln[1 + (b_2 - 1)y_{Ab}] \right)} + O(Q^{-3}) + O(\epsilon). \quad (4.38)$$

Then, the rate of change of aspect ratio is derived as

$$\frac{dA_p}{d\tau} = \frac{R(0) - R(\frac{\pi}{2})}{R^2(\frac{\pi}{2})} \times$$

$$\frac{3 \frac{\ln[1 + (b_2 - 1)y_{Ab}]}{(b_2 - 1)y_{Ab}}}{Q(1 + Q) \left(3 + Q + \frac{Q}{1+Q} \ln[1 + (b_2 - 1)y_{Ab}] \right)} + O(\epsilon Q^{-4}) + O(\epsilon^2), \quad (4.39)$$

The above two equations show the same asymptotic behavior as was found in 2.2.

Eq.'s (4.38) is shown in Figure 7 with five values of $(b_2 - 1)y_{Ab}$. Even in case of $0 < b_2 < 1$, the same u_A and $\frac{dA_p}{d\tau}$ are derived.

When y_{Ab} is very small, we can use the molecular diffusion. Also, as b_2 approaches 1, we end up with the case of the equimolar counterdiffusion where the form of mass flux equation is equivalent to the case of molecular diffusion. All the equations derived in this chapter are reduced to the counterparts of molecular diffusion for these limiting cases.

5. Boundary Integral Method.

In the case where the governing equation is the Laplace equation with a smooth boundary, by using Green's second identity we can derive

$$-2\pi u_i = \int_{\Omega} \left[u \frac{\partial g}{\partial n} - g \frac{\partial u}{\partial n} \right] dA, \quad (5.1)$$

where g is the Green's function for the Laplace equation and is expressed as follows[6].

$$g = \frac{1}{|\mathbf{x} - \xi|}. \quad (5.2)$$

The subscript i and ξ denote the position of the singularity and Ω is an arbitrary boundary of the domain. Since in our problem

$$u \rightarrow 1 \quad \text{as } |\mathbf{x}| \rightarrow \infty,$$

eq.(5.1) reduces to

$$4\pi - 2\pi u_i = \int_{\Omega_1} \left[u \frac{\partial g}{\partial n} - g \frac{\partial u}{\partial n} \right] dA \quad (5.3)$$

where Ω_1 is the smooth surface of the particle. For the procedure of derivation, see Appendix III. Since spherical coordinates are most convenient in this problem, the above equation is reduced to

$$4\pi - 2\pi u_i = \int_0^\pi \int_0^{2\pi} \left[u \frac{\partial g}{\partial n} - g \frac{\partial u}{\partial n} \right] R^2(\theta, \tau) \sin \theta d\phi d\theta. \quad (5.4)$$

And since in our problem

$$\frac{\partial u}{\partial n} = -Qu \quad \text{on the partical surface,} \quad (5.5)$$

we finally have

$$4\pi - 2\pi u_i = \int_0^\pi \int_0^{2\pi} u \left(\frac{\partial g}{\partial n} + Qg \right) R^2(\theta, \tau) \sin \theta d\phi d\theta. \quad (5.6)$$

Since we know, in the case of a spherical solid, the analytical solution which is the $O(1)$ -solution of domain perturbation, we can check eq.(5.6) by deriving the $O(1)$ -solution of domain perturbation as a special case. With a spherical particle, u is homogeneous all over the surface. It is easily confirmed that the $O(1)$ -solution of the domain perturbation is derived by using constant u and $R = 1$ in the above integral equation.

In this paper, we are restricting our problem to the axisymmetric case only. Therefore, the above equation reduces to

$$4\pi - 2\pi u_i = \int_0^\pi u \left(\frac{\partial G}{\partial n} + QG \right) R^2(\theta, \tau) \sin \theta d\theta, \quad (5.7)$$

where

$$G = \int_0^{2\pi} g d\phi. \quad (5.8)$$

For an axisymmetric case like this problem, the integration of Green's function and its normal derivative in the azimuthal direction results in complete elliptic integrals. These $\frac{\partial G}{\partial n}$ and G are expressed as follows[7].

$$\begin{aligned} \frac{\partial G}{\partial n} &= \frac{2n_r}{r(a+b)^2} [E_{3/2}(m) - E_{1/2}(m)] \\ &\quad - 4 \frac{n_r(r+r_i) + n_z(z-z_i)}{(a-b)(a+b)^{1/2}} E_{-1/2}(m) \end{aligned} \quad (5.9)$$

and

$$G = \frac{4}{(a+b)^{1/2}} E_{1/2}(m), \quad (5.10)$$

where E_k 's are elliptic integrals and m is defined as

$$m = \frac{(r - r_i)^2 + (z - z_i)^2}{(r + r_i)^2 + (z - z_i)^2}. \quad (5.11)$$

r is the distance of a point on the surface from the symmetric axis, z . E_k 's, a and b are defined as follows.

$$E_k = \int_0^{\pi/2} [1 - (1 - m) \sin^2 \phi]^{-k} d\phi. \quad (5.12)$$

$$a = r_i^2 + r^2 + (z - z_i)^2. \quad (5.13)$$

$$b = 2rr_i. \quad (5.14)$$

We solved the integral equation by approximating the radius of each point on the particle boundary linearly. We used approximating polynomials to evaluate three elliptic integrals[8]. Refer to Appendix IV for the details. We used 8-point Gaussian quadrature to evaluate the integral in the θ -direction. As we approach $m = 0$, $E_{1/2}$ and $E_{3/2}$ become singular. So, the elliptic integrals cannot be used near the singular point. Thus we calculated the surface integral around the singular point analytically using a Taylor expansion. This numerical method gave a maximum 0.05 % error in case of spherical surface.

We first calculated the surface concentrations with the shape of $R = 1 + (0.01)P_2(\eta)$ for comparison with the results from the method of domain perturbation. The two methods give almost identical results. Figure 3 shows the results from those two methods. Finally, the surface concentrations are calculated with moderate aspect ratio or eccentricity. These concentrations are shown in Figure 2.

6. Discussion.

Figure 2-6 are for the case of molecular diffusion whereas Figure 7 is for the case of binary diffusion. Figure 2 shows the dimensionless concentrations calculated from the boundary integral method with three values of eccentricity under the condition of $Q = 1$. The dimensionless concentration on the surface increases with radial distance from the origin.

Figure 3 shows the concentrations normalized by the difference between the large radius and small radius. The two solid lines are the results from the method of domain perturbation with the shape of $R(\theta, 0) = 1 + (0.01)P_2(\eta)$. The upper line is for the maximum concentration which occurs at $\theta = 0$ and the lower line is for the minimum concentration which is obtained at $\theta = \frac{\pi}{2}$. As Q becomes very large within the range where the assumption of quasi-steady state is satisfied or as it goes to zero, the concentration approaches the value of the sphere. This fact is physically reasonable because the surface concentration is uniformly close to one with very small Q whereas it is uniformly close to zero with very large Q .

Figure 4 shows dimensionless rate of change of aspect ratio. The solid line is the result from domain perturbation. Crosses are the results from the boundary integral method with the same shape. We then increased the value of eccentricity to see its effect. It turns out to have negligible effect on the curve as shown in Figure 4. So, we can say that the RHS is not a function of A_p . Therefore, from eq.(2.26) the rate of change of aspect ratio increases as the aspect ratio does under the same value of Q .

Furthermore, we know from the analysis by domain perturbation in case of

molecular diffusion the following result.

$$RHS \simeq \frac{3}{(Q+1)(Q+3)}.$$

Also, in case of binary diffusion, RHS is derived with large value of Q as

$$RHS \simeq \frac{3 \frac{\ln[1+(b_2-1)y_{Ab}]}{y_{Ab}(b_2-1)}}{(1+Q) \left(3 + Q + \frac{Q}{1+Q} \ln[1+(b_2-1)y_{Ab}] \right)},$$

which is shown as solid lines in Figure 7. In most cases $(b_2 - 1)y_{Ab}$ is between 0.5 and -0.5. Thus from Figure 7 we can find out that RHS of the binary diffusion is not much different from that of the molecular diffusion.

In both cases, we can get the asymptotic forms of RHS as follows. When Q is large enough,

$$RHS \simeq \frac{3}{Q^2} \frac{\ln[1+(b_2-1)y_{Ab}]}{y_{Ab}(b_2-1)}. \quad (6.1)$$

When Q is small enough,

$$RHS \simeq 1. \quad (6.2)$$

Therefore we get the following asymptotic results for the rate of change of aspect ratio. When the diffusion controls (Q large),

$$\frac{dA_p}{d\tau} \simeq \frac{3}{Q^3} \frac{A_p - 1}{R(\frac{\pi}{2})} \frac{\ln[1+(b_2-1)y_{Ab}]}{y_{Ab}(b_2-1)}. \quad (6.3)$$

When the reaction controls (Q small),

$$\frac{dA_p}{d\tau} \simeq \frac{1}{Q} \frac{A_p - 1}{R(\frac{\pi}{2})}. \quad (6.4)$$

thus the rate of change of aspect ratio becomes very large if the reaction controls whereas it is nearly negligible if the diffusion controls as long as the particle has not shrunk enough. Therefore the shape change is nearly negligible when Q is large

enough whereas we cannot get at this moment to the conclusion that the shape of the particle changes quickly even if Q is small enough because the reaction time is also small.

Now we need to estimate how quickly the shape of the particle changes starting with a small value of Q in case of molecular diffusion. From eq.(3.22), we get approximately

$$\tau_{max} \simeq Q_0 \quad (6.5)$$

and

$$Q \simeq Q_0 \left(1 - \frac{\tau}{\tau_{max}} \right). \quad (6.6)$$

Here τ_{max} is the necessary time for the complete reaction and it is obtained by making Q larger than zero in eq.(3.22). If we substitute the eq.'s (6.5) and (6.6) in eq.(6.4) and then solve the resulting differential equation, we get

$$A_p - 1 > (A_{p0} - 1) \frac{\tau_{max}}{\tau_{max} - \tau}. \quad (6.7)$$

For example, consider the case of $A_{p0} = 1.1$ under the condition of reaction control. From the above equation the aspect ratio becomes larger than 2 at $\tau = (0.9)\tau_{max}$.

Now let's consider about the nonisothermal effect briefly. It is assumed that the solid temperature is uniform inside the solid and that there is a thermal boundary layer between the particle and gas. In steady state we have the following heat balance on the particle surface.

$$b_1 k(T) c_{Ab} u_A (-\delta H_R) = h(T - T_b). \quad (6.7)$$

As T approaches zero, $k(T)$ also does so exponentially. On the other hand, as T becomes large, u_A goes to Q^{-1} . Then we get

$$k(T) u_A \longrightarrow \frac{D_A}{\tilde{R}_s} \quad (6.8)$$

when T is large enough. Therefore we have S-type heat generation curve as shown in Figure 8. Since the heat removal line is linear, it is possible to have one or two stable steady state temperatures of the particle depending on the values of parameters. So, it is possible to have one or two values of the rate of change of aspect ratio and we have the phenomenon of hysteresis depending on the value of Q just as in CSTR.

7. Concusions.

1. The method of domain perturbation and the boundary integral method are applied to find the concentration on the nonspherical surface of a particle undergoing a noncatalytic first order gas-solid reaction in the asymptotic case of molecular diffusion. The concentration profiles from both methods show pretty good consistency. The concentration and the mass flux on the particle surface increases with the radial distance on the surface. So, the absolute shrinking rate increases with the radial distance. However, what is related with shape change of the particle is the relative rate of shrinking, which in this case decreases with the radial distance on the surface.
2. The rate of change of aspect ratio is given in the case of molecular diffusion by

$$\frac{dA_p}{d\tau} = \frac{1}{Q(\tau)} RHS \cdot \frac{A_p - 1}{R(\frac{\pi}{2})},$$

where

$$RHS \simeq \frac{3}{(1 + Q)(3 + Q)}.$$

It turns out that the RHS is always positive and is a function of Q only. In other words, RHS does not strongly depend on the aspect ratio. So, the rate of change of aspect ratio is proportional to the geometric factor expressed as $\frac{A_p - 1}{R(\frac{\pi}{2})}$.

3. Also, the method of domain perturbation is applied to find the concentration on the slightly nonspherical surface of a particle undergoing the same reaction under the condition of diffusion control. The results obtained are asymptotically reduced to those of molecular diffusion when $(b_2 - 1)y_{Ab}$ approaches zero.
4. The rate of change of aspect ratio is given in case of binary diffusion by

$$\frac{dA_p}{d\tau} = \frac{1}{Q(\tau)} RHS \cdot \frac{A_p - 1}{R(\frac{\pi}{2})},$$

where

$$RHS \simeq \frac{3^{\frac{\ln[1+(b_2-1)y_{Ab}]}{y_{Ab}(b_2-1)}}}{(1+Q) \left(3 + Q + \frac{Q}{1+Q} \ln[1 + (b_2 - 1)y_{Ab}] \right)}.$$

with a large value of Q .

8. References

1. O. Levenspiel, *Chemical Reaction Engineering*, Wiley, New York (1972).
2. J. Szekeley, J.W. Evans and H.Y. Shon, *Gas-Solid Reactions*, Academic press, New York(1976).
3. S.H. Lee and L.G. Leal, *J. Colloid Interface Sci.***87**(1), 81(1982).
4. I.S. Kang and L.G. Leal, *J. Fluid Mech.***187**, 231(1988)
5. J.S. Kirkaldy, *Can. J. Phys.***36**, 446(1958)
6. I. Stakgold, *Boundary Value Problems of Mathematical Physics*, vol.II, Macmillan, New York(1972).
7. J.A. Liggett and P.L-F. Liu, *The Boundary Integral Equation Method for Porous media Flow*, George Allen & Unwin Ltd, London(1983).
8. M. Abramowitz and I.A. Stegun, *Handbook of mathematical Functions*, 8th ed., Dover, New York(1972).

Appendix I.

Eq.'s (2.9) and (2.10) are derived here. Suppose F defines the shape of particle. Then, F is expressed as

$$F \equiv \rho - \tilde{R}(\theta, t) \equiv 0. \quad (\text{I.1})$$

If we differentiate eq.(I.1) with respect to time, we get

$$\delta F \equiv 0 = \frac{\partial F}{\partial t} \delta t + \left(\sum_{i=1}^3 \frac{\partial F}{\partial x_i} \frac{\partial x_i}{\partial t} \right) \delta t. \quad (\text{I.2})$$

Therefore we get

$$\frac{\partial F}{\partial t} + \sum_{i=1}^3 \frac{\partial F}{\partial x_i} \frac{\partial x_i}{\partial t} = 0. \quad (\text{I.3})$$

In other words,

$$\frac{\partial F}{\partial t} + \mathbf{v}_s \cdot \nabla F = 0. \quad (\text{I.4})$$

∇F is expressed in terms of spherical coordinates as

$$\nabla F = \mathbf{i}_\rho - \mathbf{i}_\theta \frac{1}{\tilde{R}} \frac{\partial \tilde{R}}{\partial \theta}. \quad (\text{I.5})$$

Note that

$$\frac{\nabla F}{|\nabla F|} = -\mathbf{n}. \quad (\text{I.6})$$

So, we derive

$$\tilde{\mathbf{n}} = -\alpha \mathbf{i}_\rho + \beta \mathbf{i}_\theta, \quad (\text{2.10})$$

where

$$\alpha = \frac{1}{\sqrt{1 + \left(\frac{1}{\tilde{R}} \frac{\partial \tilde{R}}{\partial \theta} \right)^2}} \quad \text{and} \quad \beta = \frac{\frac{1}{\tilde{R}} \frac{\partial \tilde{R}}{\partial \theta}}{\sqrt{1 + \left(\frac{1}{\tilde{R}} \frac{\partial \tilde{R}}{\partial \theta} \right)^2}}. \quad (\text{2.11})$$

If we use eq.(I.6) in eq.(I.4), we derive

$$\frac{1}{|\nabla F|} \frac{\partial F}{\partial t} - \mathbf{v}_s \cdot \tilde{\mathbf{n}} = 0 \quad \text{on the particle surface.} \quad (\text{2.4})$$

From the mass balance,

$$\rho_s \mathbf{v}_s \cdot \mathbf{n} dA = bkcdA. \quad (\text{I.7})$$

After we substitute eq.(I.7) in eq.(2.4), we get

$$-\frac{\partial \tilde{R}}{\partial t} = \frac{bk}{\rho_s \alpha} c \quad \text{at} \quad \tilde{\rho} = \tilde{R}(\theta, t). \quad (2.9)$$

Appendix II.

By the method of domain perturbation, eq.'s (2.15) and (2.17) are expressed

as

$$\begin{aligned}
& [1 + \epsilon(2R_1) + \epsilon^2(2R_2 + R_1^2) + \dots] \left[\frac{\partial u_0}{\partial \rho} + \epsilon \left(\frac{\partial u_1}{\partial \rho} + \frac{\partial^2 u_0}{\partial \rho^2} R_1 \right) \right. \\
& \quad \left. + \epsilon^2 \left(\frac{\partial u_2}{\partial \rho} + \frac{\partial^2 u_0}{\partial \rho^2} R_2 + \frac{\partial^2 u_1}{\partial \rho^2} R_1 + \frac{1}{2} \frac{\partial^3 u_0}{\partial \rho^3} R_1^2 \right) + \dots \right] \\
& \quad - \left(\epsilon \frac{\partial R_1}{\partial \theta} + \epsilon^2 \frac{\partial R_2}{\partial \theta} + \dots \right) \\
& \times \left[\frac{\partial u_0}{\partial \theta} + \epsilon \left(\frac{\partial u_1}{\partial \theta} + \frac{\partial^2 u_0}{\partial \rho \partial \theta} R_1 \right) + \epsilon^2 \left(\frac{\partial u_2}{\partial \theta} + \frac{\partial^2 u_0}{\partial \rho \partial \theta} R_2 + \frac{\partial^2 u_1}{\partial \rho \partial \theta} R_1 + \frac{1}{2} \frac{\partial^3 u_0}{\partial \rho^2 \partial \theta} R_1^2 \right) + \dots \right] \\
& = Q \left[1 + \epsilon(2R_1) + \epsilon^2(2R_2 + R_1^2 + \frac{1}{2} \left(\frac{\partial R_1}{\partial \theta} \right)^2) + \dots \right] \\
& \times \left[u_0 + \epsilon \left(u_1 + \frac{\partial u_0}{\partial \rho} R_1 \right) + \epsilon^2 \left(u_2 + \frac{\partial u_1}{\partial \rho} R_1 + \frac{\partial u_0}{\partial \rho} R_2 + \frac{1}{2} \frac{\partial^2 u_0}{\partial \rho^2} R_1^2 \right) + \dots \right] \quad (\text{II.1})
\end{aligned}$$

and

$$\begin{aligned}
& -\frac{dQ}{d\tau} - \epsilon \left(\frac{dQ}{d\tau} R_1 + Q \frac{\partial R_1}{\partial \tau} \right) - \epsilon^2 \left(\frac{dQ}{d\tau} R_2 + Q \frac{\partial R_2}{\partial \tau} \right) - \dots = u_0 + \epsilon \left(u_1 + \frac{\partial u_0}{\partial \rho} R_1 \right) \\
& + \epsilon^2 \left[u_2 + \frac{\partial u_1}{\partial \rho} R_1 + \frac{\partial u_0}{\partial \rho} R_2 + \frac{1}{2} \frac{\partial^2 u_0}{\partial \rho^2} R_1^2 + \frac{1}{2} \left(\frac{\partial R_1}{\partial \theta} \right)^2 u_0 \right] + \dots \quad (\text{II.2})
\end{aligned}$$

So, B.C.'s for the $O(1)$ -problem are

$$\frac{\partial u_0}{\partial \rho} = Q u_0 \quad (\text{II.3})$$

and

$$-\frac{dQ}{d\tau} = u_0. \quad (\text{II.4})$$

B.C.'s for the $O(\epsilon)$ -problem are

$$\frac{\partial u_0}{\partial \rho} (2R_1) + \frac{\partial u_1}{\partial \rho} + \frac{\partial^2 u_0}{\partial \rho^2} R_1 - \frac{\partial R_1}{\partial \theta} \frac{\partial u_0}{\partial \theta}$$

$$= Q[u_1 + \frac{\partial u_0}{\partial \rho} R_1 + u_0(2R_1)] \quad (\text{II.5})$$

and

$$-(\frac{dQ_0}{d\tau} R_1 + Q_0 \frac{\partial R_1}{\partial \tau}) = u_1 + \frac{\partial u_0}{\partial \rho} R_1. \quad (\text{II.6})$$

With eq.'s (I.3) and (I.4), we can solve the $O(1)$ -problem to get

$$u_0|_{\rho=1} = \frac{1}{Q+1}, \quad (\text{II.7})$$

$$\frac{\partial u_0}{\partial \rho}|_{\rho=1} = \frac{Q}{Q+1}, \quad (\text{II.8})$$

$$\frac{\partial^2 u_0}{\partial \rho^2}|_{\rho=1} = -\frac{2Q}{Q+1}, \quad (\text{II.9})$$

$$\frac{\partial^3 u_0}{\partial \rho^3}|_{\rho=1} = \frac{6Q}{Q+1} \quad (\text{II.10})$$

and

$$\frac{\partial u_0}{\partial \theta} = 0. \quad (\text{II.11})$$

Also, note that

$$\frac{dQ}{d\tau} = -\frac{1}{Q+1}. \quad (\text{II.12})$$

Then, we get the following B.C.'s for the $O(\epsilon)$ -problem by using above results in eq.'s (II.5) and (II.6).

$$\frac{\partial u_1}{\partial \rho} - Qu_1 = \frac{Q(Q+2)}{(Q+1)} R_1. \quad (\text{II.13})$$

$$Q \frac{\partial R_1}{\partial \tau} + \frac{Q-1}{Q+1} R_1 + u_1 = 0. \quad (\text{II.14})$$

Appendix III.

We explain the procedure of derivation of eq.(4.3) here. The divergence theorem for any differentiable vector $\mathbf{v}$ is expressed as

$$\int_D \nabla \cdot \mathbf{v} d\tau = \int_{\Omega} \mathbf{v} \cdot \mathbf{n} dA. \quad (\text{III.1})$$

where D is the domain of volume integration and Ω is the boundary of D and $\mathbf{n}$ is the unit outward normal vector to D on Ω . First, $\mathbf{v}$ is defined as $U \nabla V$, where U and V are any two twice differentiable functions in D . Then,

$$\int_D (\nabla U \cdot \nabla V + U \nabla^2 V) d\tau = \int_{\Omega} U \nabla V \cdot \mathbf{n} dA. \quad (\text{III.2})$$

Secondly, $\mathbf{v}$ is defined as $V \nabla U$, so that

$$\int_D (\nabla V \cdot \nabla U + V \nabla^2 U) d\tau = \int_{\Omega} V \nabla U \cdot \mathbf{n} dA. \quad (\text{III.3})$$

Subtracting eq.(III.2) from eq.(III.3) gives

$$\int_D (U \nabla^2 V - V \nabla^2 U) d\tau = \int_{\Omega} (U \nabla V - V \nabla U) \cdot \mathbf{n} dA. \quad (\text{III.4})$$

Eq.(III.4) is called the Green's second identity.

Let

$$\nabla V \cdot \mathbf{n} = \frac{\partial V}{\partial n} \quad (\text{III.5})$$

and

$$\nabla U \cdot \mathbf{n} = \frac{\partial U}{\partial n}. \quad (\text{III.6})$$

Thus the Green's second identity is written as

$$\int_D (U \nabla^2 V - V \nabla^2 U) d\tau = \int_{\Omega} (U \frac{\partial V}{\partial n} - V \frac{\partial U}{\partial n}) dA. \quad (\text{III.7})$$

If we choose U and V such that they satisfy Laplace equation, i.e., $\nabla^2 U = \nabla^2 V = 0$, we get from eq.(III.7)

$$\int_{\Omega} (U \frac{\partial V}{\partial n} - V \frac{\partial U}{\partial n}) dA = 0. \quad (\text{III.8})$$

After this point, U is chosen the variable we want to find and V is chosen the Green's function which satisfies

$$-\nabla^2 V = 4\pi\delta(\mathbf{x} - \xi). \quad (\text{III.9})$$

Therefore V is the solution at $\mathbf{x}$ when a unit source is put on ξ . If we require that V be spherically symmetric and vanish at $|\mathbf{x}| = \infty$, we find the unique solution

$$V(\mathbf{x}|\xi) = \frac{1}{|\mathbf{x} - \xi|} \equiv g \quad (\text{III.10})$$

in three dimension.

Since ξ is a singular point for V , we must remove that point from the domain of integration when we use eq.(III.8). Then

$$\int_{\Omega+\sigma} (u \frac{\partial g}{\partial n} - g \frac{\partial u}{\partial n}) dA = 0, \quad (\text{III.11})$$

where σ denotes small surface used to exclude the singular point ξ from the domain D . Eq.(III.11) is written as

$$\int_{\Omega} (u \frac{\partial g}{\partial n} - \frac{\partial u}{\partial n}) dA + \lim_{R_0 \rightarrow 0} \int_{\sigma} [u(-\frac{1}{R_0^2}) \frac{\partial R}{\partial n} - \frac{1}{R_0} \frac{\partial u}{\partial n}] dA = 0, \quad (\text{III.12})$$

where R_0 is the radius of the excluded volume. Since $\mathbf{n}$ is an outward unit normal vector,

$$(\frac{\partial R}{\partial n})_{R=R_0} = -1. \quad (\text{II.13})$$

By the way, because $\frac{\partial u}{\partial n}$ should be finite,

$$\lim_{R_0 \rightarrow 0} \int_{\sigma} \frac{1}{R_0} \frac{\partial u}{\partial n} dA = 0. \quad (\text{III.14})$$

Furthermore,

$$\lim_{R_0 \rightarrow 0} \int_{\sigma} u \left(-\frac{1}{R_0^2} \right) \frac{\partial R}{\partial n} dA = u(\xi) \lim_{R_0 \rightarrow 0} \left(\frac{A_s}{R_0^2} \right). \quad (\text{III.15})$$

Let

$$\alpha = \lim_{R_0 \rightarrow 0} \left(\frac{A_s}{R_0^2} \right). \quad (\text{III.16})$$

Here, α is the solid angle of the volume excluded from the domain. Then, in case the singular point ξ is in the domain, we get the following general integral equation.

$$-\alpha u_i = \int_{\Omega} \left(u \frac{\partial g}{\partial n} - g \frac{\partial u}{\partial n} \right) dA. \quad (\text{III.17})$$

If the singular point ξ has an interior point, the area A_s is $4\pi R_0^2$ and eq.(.) becomes

$$-4\pi u_i = \int_{\Omega} \left(u \frac{\partial g}{\partial n} - g \frac{\partial u}{\partial n} \right) dA. \quad (\text{III.18})$$

Therefore, when both u and $\frac{\partial u}{\partial n}$ are known everywhere on the boundary, eq.(III.18) gives us the value of u at an interior point ξ of domain. And now put the singular point ξ right on the boundary. If the boundary is smooth at the point ξ , the surface area excluded is $2\pi R_0^2$ and the solid angle α is 2π . So,

$$-2\pi u_i = \int_{\Omega} \left(u \frac{\partial g}{\partial n} - g \frac{\partial u}{\partial n} \right) dA. \quad (\text{III.19})$$

Eq.(III.19) is the equivalent integral equation of any Laplace equation of which the domain has smooth boundary.

Now let's simplify eq.(III.19) by applying that equation to our problem. Our problem has a constant boundary condition at infinity. We may deal with this boundary condition if we make a fictitious large sphere surrounding the particle and let the radius of that sphere go to infinity. Refer to Figure 8. Thus our boundary Ω is separated into two boundaries, Ω_1 and Ω_2 . Ω_1 is the real boundary

of particle whereas Ω_2 is the boundary of the fictitious sphere, the center of which is at the singular point, ξ . Therefore,

$$\int_{\Omega} \left(u \frac{\partial g}{\partial n} - g \frac{\partial u}{\partial n} \right) dA = \int_{\Omega_1} + \lim_{R_{\infty} \rightarrow \infty} \int_{\Omega_2}. \quad (\text{III.20})$$

Furthermore since with our problem

$$u \rightarrow 1 \quad \text{as } |\mathbf{x}| \rightarrow \infty,$$

$$\begin{aligned} \lim_{R_{\infty} \rightarrow \infty} \int_{\Omega_2} &= \lim_{R_{\infty} \rightarrow \infty} \int_{\Omega_2} \left[u \left(-\frac{1}{R_{\infty}^2} \right) - \frac{1}{R_{\infty}} \frac{\partial u}{\partial n} \right] dA \\ &= -4\pi - \lim_{R_{\infty} \rightarrow \infty} \int_{\Omega_2} \frac{1}{R_{\infty}} \frac{\partial u}{\partial n} dA. \end{aligned} \quad (\text{III.21})$$

Note any harmonic function which goes to 1 at infinity can be written for sufficiently large ρ in the form

$$1 + \sum_{n=0}^{\infty} \sum_{m=-n}^n b_{mn} \rho^{-n-1} Y_n^m(\theta, \phi). \quad (\text{III.22})$$

Therefore,

$$u|_{R_{\infty}} = 1 + O\left(\frac{1}{R_{\infty}}\right) \quad (\text{III.23})$$

and

$$\frac{\partial u}{\partial n}|_{R_{\infty}} = O\left(\frac{1}{R_{\infty}^2}\right). \quad (\text{III.24})$$

So,

$$\lim_{R_{\infty} \rightarrow \infty} \int_{\Omega_2} \frac{1}{R_{\infty}} \frac{\partial u}{\partial n} dA = 0. \quad (\text{III.25})$$

In conclusion, we get eq.(4.3) as follows.

$$4\pi - 2\pi u_i = \int_{\Omega_1} \left[u \frac{\partial g}{\partial n} - g \frac{\partial u}{\partial n} \right] dA. \quad (\text{III.26})$$

Appendix IV.

When the singular point is not included in a boundary element, the complete elliptic integrals are approximated by the following polynomials for the convenience of numerical computations.

$$E_{1/2}(m) = \sum_{k=0}^4 a_k m^k + \sum_{k=0}^4 b_k m^k \ln(1/m) + \epsilon(m) \quad (\text{IV.1})$$

$$E_{-1/2}(m) = \sum_{k=0}^4 c_k m^k + \sum_{k=1}^4 d_k m^k \ln(1/m) + \epsilon(m) \quad (\text{IV.2})$$

$$E_{3/2}(m) = \frac{E_{-1/2}}{m} \quad (\text{IV.3})$$

$$\epsilon \leq 2 \times 10^{-8}$$

$a_0 = 1.38629436112$	$b_0 = 0.5$
$a_1 = 0.09666344259$	$b_1 = 0.12498593597$
$a_2 = 0.03590092383$	$b_2 = 0.06880248576$
$a_3 = 0.03742563713$	$b_3 = 0.03328355346$
$a_4 = 0.01451196212$	$b_4 = 0.00441787012$

$c_0 = 1.0$	
$c_1 = 0.44325141463$	$d_1 = 0.24998368310$
$c_2 = 0.06260601220$	$d_2 = 0.09200180037$
$c_3 = 0.04757483546$	$d_3 = 0.04069697526$
$c_4 = 0.01736506451$	$d_4 = 0.00526449639$

Figure 1. Simplified schematic of domain

Figure 2. Variation of surface concentration with θ
when $Q=1$

Figure 3. Variations of maximum and minimum surface concentrations with Q .

Figure 4. Rate of change of aspect ratio vs. Q for various shapes.

Figure 5. Rate of change of aspect ratio vs. Q for various shapes.

Figure 6. The rate of change of aspect ratio vs. Q .

Figure 7. The rate of change of aspect ratio vs. Q in case of binary diffusion.

Figure 8. Singular point and boundaries.