3) The addition of generation means that the maximum or minimum value of our state variable need not occur on the boundary, but may often occur somewhere inside the system.

In the next few sections, we will look at some more complicated examples of generation and allow the generation term to be a function of the dependent variable. This will let us look at some more realistic problems including diffusion with homogeneous chemical reaction, natural convection, and the operation of a transistor.

5.5 Variable Generation and Coupled Transport

We have considered cases where the generation term was a constant quantity. Often nature is not that simplistic and the generation term varies as a function of position, time, or one of the state variables of our system. In this section we will consider a few of the more common examples of variable generation and show how the generation term can couple transport processes much as the variable transport coefficients did in Chapter 4.

5.5.1 Simultaneous Diffusion and Reaction

Our first example of variable generation and coupled transport involves diffusion, an exothermic chemical reaction, and heat generation in a fluid system. The physical situation is shown in Figure 5.12. Two immiscible fluids are in contact. Fluid I is denser and is well mixed. The concentration of species $a$ is $c_{a0}$ everywhere within this fluid and the temperature in fluid I is held constant at $T_0$. Species $a$ diffuses through stagnant fluid II and undergoes a first-order reaction $(a \rightarrow b)$ with the fluid.

We assume constant properties in both phases. The reaction occurs with a rate constant, $k^*$, and is exothermic, yielding $\Delta H$, joules per mole of $a$ reacted. The whole system is insulated from the surroundings and all sides of the vessel are impermeable to both fluids. We want to predict both the concentration distribution and the temperature distribution in the system. To simplify the problem to something manageable we will assume that solute $a$ is only sparingly soluble in fluid II (partition coefficient of $K_{\text{eq}}$). This means the temperature differences are not great enough to set up any thermally induced diffusive effects or any density driven convective effects. To determine the temperature and concentration profiles, we need to construct two balances; one for continuity of species $a$ and one for energy transport through the system. Using the control volumes set up in Figure 5.12 the mass balance on species $a$ is:
Figure 5.12 Diffusion and reaction in an insulated fluid system.

\[ \text{In} - \text{Out} + \text{Gen} = \text{Acc} \]
\[ \dot{M}_a(x) - \dot{M}_a(x+\Delta x) - k^c c_a A_c \Delta x = 0 \]  \hspace{1cm} (5.66)

Notice that the generation term involves the reaction rate multiplied by the volume of the control volume. Factoring out the constant cross sectional area, and performing the limiting process with respect to \( x \) gives:

\[ \frac{dN_a}{dx} = -k^c c_a = 0 \]  \hspace{1cm} (5.67)

Since \( a \) forms a dilute solution in fluid II, we can approximate the flux as:

\[ N_a = -D_{ab} \frac{dc_a}{dx} \]  \hspace{1cm} (5.68)

The final form for the continuity equation is:

\[ \frac{d^2c_a}{dx^2} + k^c c_a = 0 \]  \hspace{1cm} (5.69)

with boundary conditions:
These boundary conditions reflect the well-mixed system in fluid I, and that species \( a \) cannot travel through the vessel wall at \( x = L \).

The energy balance is:

\[
\text{In} - \text{Out} + \text{Gen} = \text{Acc}
\]

\[
q(x) - q(x+\Delta x) + k''c_a(-\Delta H_f)A_c\Delta x = 0
\]  \hspace{1cm} (5.72)

Following the limiting procedure yields the differential equation for the heat flow:

\[
-\frac{dq}{dx} + k''c_a(-\Delta H_f)A_c = 0
\]  \hspace{1cm} (5.73)

The generation term in the energy equation depends upon the reaction rate and hence upon the solution to the mass transfer problem. We use Fourier's law to transform the differential equation in terms of the temperature.

\[
\frac{d^2 T}{dx^2} + \frac{k''(-\Delta H_f)}{k}c_a = 0
\]  \hspace{1cm} (5.74)

The boundary conditions for the heat transform problem are direct analogs of the boundary conditions we used in our balance on \( a \):

\[
x = 0 \quad T = T_o
\]  \hspace{1cm} (5.75)

\[
x = L \quad \frac{dT}{dx} = 0
\]  \hspace{1cm} (5.76)

and reflect the uniformity of fluid I and that the vessel walls are insulated.

It is often very useful to put the conservation equations in dimensionless form. This procedure simplifies the boundary conditions, forces the problem to extend over a range between 0 and 1 and leads to groupings of system parameters that have particular physical significance. We can put the balance equations for this problem in dimensionless form by defining three new variables:

\[
\chi = \frac{c_a}{K_{eq}c_{a0}} \quad \theta = \frac{T - T_o}{T_o} \quad \xi = \frac{x}{L}
\]  \hspace{1cm} (5.77)
We use the chain rule for differentiation to translate from our regular variables, \( c_p, T, \) and \( x, \) to these new dimensionless ones. Examples of this procedure for \( \frac{dc_a}{dx} \) and \( \frac{d^2T}{dx^2} \) are:

\[
\frac{dc_a}{dx} = \frac{d\xi}{dx} \cdot \frac{dc_a}{d\xi} \cdot \frac{d\xi}{dx} = \frac{dx}{d\xi} \left( \frac{K_{eq}c_{a0}}{L} \right)
\]

\[
\frac{d^2T}{dx^2} = \frac{d}{d\xi} \left( \frac{dT}{d\xi} \cdot \frac{d\xi}{dx} \right) \cdot \frac{d^2\xi}{dx^2} = \frac{d^2\theta}{dT} \left( \frac{T_c}{L^2} \right)
\]

The transformed equations now become:

\[
\frac{d^2\chi}{d\xi^2} - \left[ \frac{k''L^2}{D_{ab}} \right] \chi = 0 \quad \text{mass balance} \quad (5.80)
\]

\[
\frac{d^2\theta}{d\xi^2} + \left[ \frac{k''c_{eq}L^2(-\Delta H_f)}{kT_0} \right] \chi = 0 \quad \text{energy balance} \quad (5.81)
\]

The boundary conditions are similarly transformed to read:

\[
\begin{align*}
\xi = 0 & \quad \chi = 1 & \quad \theta = 0 & \quad (5.82) \\
\xi = 1 & \quad \frac{d\chi}{d\xi} = 0 & \quad \frac{d\theta}{d\xi} = 0 & \quad (5.83)
\end{align*}
\]

As promised, the procedure yields two dimensionless quantities.

\[
\frac{k''L^2}{D_{ab}} = \frac{\text{Damkohler Number}}{(Da)}
\]

\[
\frac{k''(-\Delta H_f)K_{eq}c_{a0}L^2}{kT_0} = \frac{\text{Generation Number}}{(Gn)}
\]

The Damkohler number reflects the competition between the rate at which species \( a \) is supplied to fluid \( II \) by diffusion and the rate at which that species is consumed in fluid \( II \) by the reaction. High Damkohler numbers imply that the reaction rate is so fast we cannot supply enough of species \( a \) to satisfy it. We refer to this situation as mass transfer controlled. Low Damkohler numbers im-
ply that the system is controlled by how fast we can consume species $a$. We refer to this regime as reaction rate controlled.

The generation number, $G_n$, reflects the competition between the amount of heat generated by the reaction and the amount of heat that can be removed from the system via conduction. High generation numbers imply the heat flow in the system is controlled by the amount of heat generated. Exothermic reaction systems with high generation numbers and high reaction rates tend to be unstable. Small generation numbers imply that the system can remove more heat than can be generated. Endothermic reaction systems with small generation numbers are much more stable.

The two balance equations are coupled. To solve for the concentration profile and the temperature profile, we must first solve the mass balance for the concentration field. The general solution to equation (5.80) cannot be obtained by separating and integrating. It is found by substituting a trial solution, $Ae^{x}$ into the equation. This procedure yields a quadratic equation for $r$.

$$r^2 - Da = 0 \quad r = \pm \sqrt{Da} \quad (5.86)$$

The solution can be written as exponentials or the exponentials can be arranged in the form of hyperbolic sine and hyperbolic cosine functions.

$$\chi = a_1 \cosh(\sqrt{Da} \xi) + a_2 \sinh(-\sqrt{Da} \xi) \quad (5.87)$$

According to our boundary conditions,

![Figure 5.13](image-url)

Figure 5.13 Concentration and temperature profiles in fluid II of Figure 5.12. Since $G_n / Da > 1$ the temperature increases faster than the concentration decreases.
Generation
\[ \xi = 0 \quad \chi = 1 \quad \rightarrow \quad a_1 = 1 \]  
(5.88)
\[ \xi = 1 \quad \sqrt{Da} \sinh(\sqrt{Da}) + a_2 \sqrt{Da} \cosh(\sqrt{Da}) = 0 \]
\[ a_2 = -\tanh(\sqrt{Da}) \]  
(5.89)

Using these constants, the concentration profile is:
\[ \chi = \cosh(\sqrt{Da} \xi) - \tanh(\sqrt{Da}) \sinh(\sqrt{Da} \xi) \]  
(5.90)

The temperature profile can now be obtained by substituting for \( \chi \) in equation (5.81). The resulting differential equation can be separated and integrated twice to yield:
\[ \theta = -\frac{Gn}{Da} \left[ \cosh(\sqrt{Da} \xi) - \tanh(\sqrt{Da}) \sinh(\sqrt{Da} \xi) \right] + a_3 \xi + a_4 \]  
(5.91)

Using the boundary conditions (equations (5.82) and (5.83)), we find that:
\[ a_3 = 0 \quad a_4 = \frac{Gn}{Da} \]  
(5.92)

and the resulting temperature profile is:
\[ \theta = \frac{Gn}{Da} \left[ 1 - \cosh(\sqrt{Da} \xi) + \tanh(\sqrt{Da}) \sinh(\sqrt{Da} \xi) \right] \]  
(5.93)

The full concentration and temperature profiles are shown in Figure 5.13. For convenience, the generation number, \( Gn \) is 2, and the Damkohler number, \( Da \) is 1. Since the ratio of \( Gn \) to \( Da \) is greater than one, the temperature profile is steeper than the concentration profile.

Example: Simultaneous Diffusion and Enzymatic Reaction

We can use a system, like that shown in Figure 5.12 to run an enzymatic reaction for producing a drug, foodstuffs, or ethanol for car fuel. The only difference between an enzymatic reaction and the first order reaction we just analyzed is the nature of the kinetic expression. Most enzymatic reaction obey Michaelis-Menten kinetics and are inhibited by high concentrations of the reactant. The rate of the enzymatic reaction can be modeled as: