EQUATIONS OF HEAT CONDUCTION WITH SLOW COMBUSTION

by

Graeme C. WAKE, M.Sc.(Vict.)

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ERRATA

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The following are noted.

p.22. Line five. A better proof can be given:

"Suppose $a > b$, then

$$\frac{a^\beta - b^\beta}{a - b} = \frac{\beta}{h}\int_b^a x^{\beta-1}dx = \beta\ \xi^{\beta-1} \quad \text{for some} \quad \xi \in (b,a) ,$$

where $h = a - b$. Then the expression is less than or equal to $\beta R^{\beta-1}$."

p.23. Line four from bottom. Reverse inequality.

p.30 Line nine, should read ... "For t large and negative, p,q" ...

p.31. Figure 3.2. The singularity is stable, and thus the arrows should be directed towards the origin and not away from it.

p.44. Line three from bottom. Refers to a note on p.5 and not p.6.

p.45 Line six. A negative sign instead of a positive sign should be inserted before the last term in G_2.

p.47. Equation (4.8). Omit "8", also from " $e^{-y^2}/8\pi^{\frac{1}{2}}y^3 = s$".

p.48. Equation (4.9), should read " $\Theta = t(4z/\pi^{\frac{1}{2}} - 2z^2 - 2z^3/3\pi^{\frac{1}{2}} \ldots)$".

p.61-2. Equations (5.12),(5.14). Omit "a" from both equations.

p.77. Equation (6.18). The first term on the right hand side should be " $\frac{1}{z^3}$ " not " $\frac{1}{z^2}$" .

p.79. Line fourteen, should read ... "be chosen as the positive alternative, which ..."

p.79. Bottom of page. The second contour chosen clearly satisfies the criterion imposed. The form given for the corresponding solution is that obtained by letting the radius of the circle about the origin, say ε, tend to zero. This does give a solution of the differential equation (6.25) since the second derivative of G is uniformly convergent as $\varepsilon \to 0$, for each $s \geqslant 0$. The details have been omitted.

p.79. Line two from bottom. Insert the curly bracket before e^{-rs} and not after in the integrand.

p.88. Line five from bottom. This should read ..."then obviously $\{\theta_n\}$ is an equicontinuous set of functions...".

ABSTRACT

A study is made of the equations of heat conduction with slow combustion. A mathematical model is established from an interpretation of the physical model, with a few simplifying assumptions. This gives rise to a coupled pair of partial differential equations which are the direct concern of this thesis, the dependent variables being the temperature and reactant concentration as functions of position and time.

The model is shown to possess a unique solution for which some properties, such as Lipschitz conditions etc., are established. An investigation into the use of a comparison theorem is given, in which it is shown that no direct comparison theorem is possible for this and related systems. However, it is also shown that it is possible to obtain upper and lower estimates by appealing to the physical model.

A discussion of the boundary layer is given and this is followed by a detailed discussion of stability. The latter has been one of the main concerns of earlier authors on this system. Their use of a space-averaging process to establish a criterion for stability is also discussed.

Probably one of the most interesting features of this system is the subclass of problems for which the reactant is exhausted in a finite time. These have been named the "cut-off" problems and they can be likened to the free boundary problems in fluid dynamics. A discussion of the cut-off problem is given with particular examples chosen to illustrate the main features.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University and to the best of my knowledge and belief, the thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

G.C. Wake.

G.C. Wake.

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G.C. Wake.

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INTRODUCTION

This thesis is concerned with the diffusion of heat in a given material which is undergoing internal combustion. The material contains reactant which is consumed by this combustion, and heat is produced. It is assumed that both the thermal conductivity and capacity of the material as a whole are unchanged by this process. The heat thus produced, is conducted through the material and so gives rise to a corresponding temperature increase and enhances the reaction rate. It is the intention of this thesis to set up a mathematical model for this phenomenon and to show that there exists a unique solution, which does in fact represent the temperature and reactant concentration. Considerable attention will be given to particular examples which illustrate many of the qualitative aspects of the problem.

Recently the problem has received considerable attention and an extensive literature on this and related problems has accumulated. A comprehensive account of some of the earlier work is given in Frank-Kamenetskii [1]. This work is confined to reactions in which the rate at which the reaction proceeds is independent of how much reactant is present at any time (such reactions are called zero order reactions). This problem, by no means a trivial one, is nonetheless a much easier one to solve. For there is now just one dependent variable, that of the temperature which is obtained as a function of position and time. However in the general case, in which the reaction rate does depend on the reactant concentration (say to the nth power), there is a coupling effect in the differential equations. That is, there are two dependent variables, that of the temperature and reactant concentration, both of which appear in each differential equation.

Frank-Kamenetskii derives the steady-state solution for a zero order reaction in one dimension and examines the conditions under which it is possible to obtain such a solution. The extreme conditions under which this is possible are called the critical conditions. Chambre [2] contains a similar treatment for two dimensional problems. Later work [3,4] has been generalised to a nth order reaction, i.e. one in which the reaction rate depends on the nth power of the reactant concentration. Both of these authors have used space-averaged temperatures, i.e. have converted what were partial differential equations into ordinary differential equations in time.

The author was introduced to this problem in connection with the self-heating of wool. This has been a subject of study for a number of years in New Zealand, and the prevention of spontaneous combustion in wool has an obvious relevance to the export trade of this country. Many experiments have been carried out to determine the temperature rises that actually do occur under various conditions. The results of these and many associated calculations are available in Walker et al [5,6]. Different shapes are used, for example cylindrical, spherical etc. The difficulty of obtaining solutions for these shapes generally increases with the geometry of the material. This is seen to be so, for in the case of a zero order reaction, such as that discussed by Frank-Kamenetskii and Chambre, no equivalent exact solution can be obtained in three dimensions. In Wake and Walker [7], use is made of the numerical solution of the problem for a sphere to calculate the central temperature rises in geometries which are mathematically less tractable than that of the former.

The approach presented here will be more qualitative, though many examples will be given. After setting up the model, further comments will be made on the space-averaging process. (See Chapter 5).

1.1 Definition of the Model

The rate at which the reactant proceeds is measured by the rate at which the reactant is consumed. If λ denotes the reactant concentration as a function of position (x) and time (t), then

$$\frac{\partial \lambda}{\partial t} = - g(x,\theta,\lambda), \qquad \ldots . (1.1)$$

where θ denotes the temperature. The fact that this rate is also a function of position reflects the possibility of a catalyst being present within the material. An nth order reaction is one in which a term λ^n occurs in the right-hand side of equation (1) ‡. In much of the literature use is made of the Arrhenius equation

$$\frac{\partial \lambda}{\partial t} = - A \lambda^n e^{-B/\theta}, \qquad \ldots . (1.2)$$

where A and B are constants.

---

‡ Reference to equations in the same chapter will not include the chapter number associated with the number of the equation.

The rate at which heat is produced per unit volume likewise can be written

$$Q = F(x,\theta,\lambda). \quad \ldots . (1.3)$$

This quantity Q is directly proportional to $\frac{\partial\lambda}{\partial t}$. The factor of proportionality is, in general, a function of temperature, since the amount of heat produced by a given amount of reactant depends on the temperature at which it is consumed. However, the authors previously mentioned[3,4] have implied that Q is in fact equal to a constant multiple of $\frac{\partial\lambda}{\partial t}$. Therefore it must be recognized that in writing

$$Q = -\alpha\frac{\partial\lambda}{\partial t} \quad \ldots . (1.4)$$

where α is a constant, that an approximation has been made. To be precise it is assumed that this proportionality factor can be regarded as constant for the temperature range concerned. This assumption will be made with many of the examples which are discussed herein, but it is to be remembered that there is this restriction to the fitting of the analysis to any particular problem.

The medium is assumed to be of q dimensions, that is, x denotes a vector in the cartesian space of that dimension. The heat produced by the combustion of reactant diffuses through the medium according to the equation

$$k\Delta\theta + Q = C\frac{\partial\theta}{\partial t}, \quad \ldots . (1.5)$$

where k and C are the thermal conductivity and capacity of the material respectively, both being constants. Δ is the Laplacian in q dimensions, i.e.

$$\Delta\theta = \sum_{i=1}^{q} \frac{\partial^2\theta}{\partial x_i^2} \quad \ldots . (1.6)$$

Equation (5) can be written

$$\Delta\theta - \frac{1}{\kappa}\frac{\partial\theta}{\partial t} = f(x,\theta,\lambda) , \qquad \ldots . (1.7)$$

where $\kappa = k/C$, is the thermal diffusivity of the material. Thus there is the coupled pair of partial differential equations (1) and (7) to be solved with prescribed initial and boundary conditions. Obviously the initial reactant concentration and temperature variation can be specified. Further a boundary condition on the temperature and its first derivatives with respect to x is given. The latter corresponds to whatever physical condition is imposed on the surface of the material. The most usual of these are the following:

1. Prescribed surface temperature, which may be a function of time.

2. Thermal insulation i.e. zero heat flux on the surface, which means $\frac{\partial\theta}{\partial N} = 0$ on all points of the surface. $\partial/\partial N$ denotes differentiation in the direction of the outward normal to the surface.

3. Radiation at the surface, where the flux across the surface is assumed to be proportional to the temperature difference between the surface and the surrounding medium, i.e. $k\frac{\partial\theta}{\partial N} + h(\theta - \theta_o) = 0$ on all points of the surface. The quantity h is called the coefficient of surface heat transfer. As $h \to 0$ this tends to the boundary condition 2, and as $h \to \infty$ it tends to the condition 1.

If the rate of reaction does not depend on the reactant concentration then an immediate simplification occurs. Equation (7) becomes a quasi-linear equation for the dependent variable θ. This is the case investigated in Frank-Kamenetskii[1], with the rate of heat production given in the Arrhenius equation (2) with $n = 0$. No attempt was made in this work to discuss the implications of the reactant becoming exhausted. The reason beimg of course, that Frank-Famenetskii was interested in the critical state and hence in times long before much reactant was consumed. However, consideration will be given to this problem here (with general n) and it will be seen that a criteria for establishing the types of reactions for which this does occur can be obtained.

In the next chapter, the existence and uniqueness of the solution is proved. This is followed by a discussion of comparison functions and reference is made to the boundary layer in Chapter 4. An explanation is offered of the work of Thomas[3] and Enig[4] (in which the idea of space-averaged temperatures was exploited) in Chapter 5, where a discussion of critical states is given also. Finally, a detailed discussion of a particular cut-off problem is given in Chapter 6.

Chapter 2

EXISTENCE AND UNIQUENESS OF SOLUTION

Not all differential equations have solutions. If a meaningful physical problem has been correctly formulated mathematically as a differential equation, then it should have a solution. Thus the question of existence arises. Further if a solution does exist, what of other possible solutions? And so the question of uniqueness arises also. It is intended to establish the existence and uniqueness of the solutions under conditions to be prescribed, and deduce certain properties of these solutions.

The equations to be discussed are, of course, those of (1.1) and (1.7) but it is intended to write these more generally so as to include more general situations. There are however, certain requirements which are suggested by this particular problem, as described in Chapter 1. The functions $f(x,\theta,\lambda)$ and $g(x,\theta,\lambda)$ are required to be bounded functions of their arguments over any finite range. They will also be continuous functions of their arguments, with the exception of a zero reaction, if and when the reactant concentration (λ) became zero. In this case f and g will have finite discontinuities when $\lambda = 0$, since obviously no heat can be produced and no further reactant can be consumed once this has occurred.

The differential equations will be written as:

$$L(\theta) \equiv \sum_{i,j}^{q} a_{ij}(x,t)\frac{\partial^2\theta}{\partial x_i \partial x_j} + \sum_{i=1}^{q} b_i(x,t)\frac{\partial\theta}{\partial x_i} + c(x,t)\theta - \frac{\partial\theta}{\partial t} = f(x,t,\theta,\lambda) \quad \ldots . (2.1)$$

$$\frac{\partial\lambda}{\partial t} = g(x,t,\theta,\lambda) \quad \ldots . (2.2)$$

The domain of the space variables will be denoted by B. This describes the volume in q dimensions occupied by the medium in which the equations (2.1) and (2.2) apply. It can be seen that the above can be specialized to the problem as posed in Chapter 1 by writing κt as t, -g for g;

$$\text{letting} \quad a_{ij} = \delta_{ij} \;, \quad \text{all } i,j$$
$$b_i = 0 \;, \quad \text{all } i$$
$$c = 0 \;;$$

and supposing that f and g are independent of time. One reason that the equations are written in this more general way, is that this would be the first step to generalizing to a more realistic situation in which the thermal properties of the medium depended on the temperature and reactant concentration.

The source term (-f) generally will be positive as the combustion is exothermic. Also the source will be a nondecreasing function of temperature, since the rate at which heat is produced increases with, or is unaffected by, temperature. Further the source will be nondecreasing with the reactant concentration, for it usually depends on λ like λ^n where $n \geqslant 0$. Similarly g will be negative for the reactant concentration decreases as the reaction proceeds. Also the reaction rate (-g) is nondecreasing with temperature and reactant concentration. Hence in this particular problem, the functions f and g in equations (1) and (2) will be nondecreasing in θ and λ. This is a very useful fact for it is possible to generate a sequence of bounds for the quantities θ and λ. For, if an upper bound is inserted for λ in equation (1) (i.e. more reactant is supposed to be present than there is in reality), then there is a greater source and hence an upper bound is obtained for θ. Likewise if an upper bound is substituted for θ in equation (2) (i.e. the temperature is supposed to be hotter than it actually is), then there is a faster consumption of reactant and hence a lower bound is obtained for λ. This approach can be used to demonstrate the existence of solutions to the equations. However, though it is intended to discuss this further, a much less restrictive proof can be given.

A very similar system is examined in McNabb[10] in which f was required to be nonincreasing in λ and g nondecreasing in θ. McNabb set up comparison theorems (which will be discussed later) and using these, he established the existence and uniqueness of solutions with these conditions. An apparently more general system is discussed in Zeragija[11], that is a system of m coupled parabolic partial differential equations,

$$\frac{\partial u_i}{\partial t} - \Delta u_i = f_i(x,t,u_1, \ldots, u_m) , \qquad \ldots . (2.3)$$

for $i = 1, \ldots, m$. Zeragija has set up comparison theorems and deduced the existence and uniqueness of the solutions of the equations (3). However, the conditions which he has imposed on the functions f_i, viz.

$$|f_i(x,t,u_1, \ldots, u_m) - f_i(x,t,u_1', \ldots, u_m')| < K|u_i - u_i'|,$$

imply that f_i is independent of each u_j for $i \neq j$. This means that the system of equations are in effect uncoupled and the results are merely applicable to the equation

$$\frac{\partial u}{\partial t} - \Delta u = f(x,t,u).$$

2.1 Preliminary Definitions

Let B be a bounded q-dimensional domain of real variables and $D_T = \{(x,t) : x \in B, \; 0 < t \leq T\}$. Further denote the boundary of B by ∂B and S_T as the cylinder $\{(x,t) : x \in \partial B, \; 0 < t \leq T\}$. If u(x,t) is defined in a given domain D, then for $0 < \alpha < 1$ the following definitions will be made:

$$|u|_o^D = \sup_{(x,t)\in D} |u(x,t)| , \qquad \ldots . (2.4)$$

$$H_\alpha^D(u) = \sup_{P,Q\in D} \frac{|u(P) - u(Q)|}{[d(P,Q)]^\alpha} , \qquad \ldots . (2.5)$$

$$|u|_\alpha^D = |u|_o^D + H_\alpha^D(u) , \qquad \ldots . (2.6)$$

where,

$$d(P,Q) = (|x-x'|^2 + |t-t'|)^{1/2} \text{ if } P = (x,t) \text{ and } Q = (x',t').$$

$H_\alpha^D(u)$ is called the Hölder coefficient of u in D.

If u is differentiable, define

$$|u|_{1+\alpha}^D = |u|_\alpha^D + \sum_{i=1}^q \left|\frac{\partial u}{\partial x_i}\right|_\alpha^D , \qquad \ldots . (2.7)$$

$$|u|_{2+\alpha}^D = |u|_{1+\alpha}^D + \sum_{i=1}^q \left|\frac{\partial u}{\partial x_i}\right|_{1+\alpha}^D + \left|\frac{\partial u}{\partial t}\right|_\alpha^D , \qquad \ldots . (2.8)$$

$$|u|_1^D = |u|_o^D + L^D(u) , \qquad \ldots . (2.9)$$

where,

$$L^D(u) = \sup_{P,Q\in D} \frac{|u(P) - u(Q)|}{|x-x'| + |t-t'|} . \qquad \ldots . (2.10)$$

$L^D(u)$ is the Lipschitz coefficient of u in D. If $|u|_p^D$ exists, then it is said that u is of class C^p. If $u \in C^1$ and $\partial u/\partial x_i \in C^1$ for all i, then it is said that $u \in C^2$. Note $u \in C^1$ does not imply that u is everywhere differentiable.

A surface S is said to be of class C^p if S can be locally represented in the form

$$x_i = X(x_1, .., x_{i-1}, x_{i-1}, .., x_q, t) \qquad \dots . (2.11)$$

for some i and the functions X are of class C^p. The surface S is covered by a finite number of neighbourhoods S_j each of which has a fixed global representation of the form (11) with X of class C^p. The quantity $|u|_p^S$ is then interpreted as the maximum of $|u|_p$ taken over all these neighbourhoods.

The following assumptions are made on the partial differential operator $L(\theta)$ of equation (1).

I. L is of parabolic type in $\overline{D}_T$. That is, there exists a positive number H_o such that for all $(x,t) \in \overline{D}_T$ and any real vector ξ, $\sum_{i,j} a_{ij}\xi_i\xi_j \geqslant H_o \sum_i \xi_i^2$.

II. a_{ij}, b_i, and c are of class C^α (for some $0<\alpha<1$) in $\overline{D}_T$, and in addition a_{ij} are of class C^1.

The functions f and g will be required to satisfy the Lipschitz condition for each (x,t) in $\overline{D}_T$,

$$|h(x,t,\theta_1,\lambda_1) - h(x,t,\theta_2,\lambda_2)| \leqslant M(|\theta_1 - \theta_2| + |\lambda_1 - \lambda_2|) \dots . (2.12)$$

Further they will be required to satisfy the Lipschitz condition

$$|h(x,t,\theta,\lambda) - h(x_1,t_1,\theta,\lambda)| \leqslant K(|x - x_1| + |t - t_1|) \quad \dots . (2.13)$$

for each fixed value of θ and λ. In (12) and (13), $h \equiv f$ or g.

The initial and boundary conditions of the temperature and reactant concentration are prescribed. Since λ satisfies a first order differential equation in t, the initial value of λ is specified when t = 0. The temperature θ, which satisfies a second order partial differential equation, will need to be specified on ∂B $(t > 0)$ as well as on $\bar{B}$ initially. These conditions, which physically are just what can be fixed, are sufficient to show that there exists a unique solution. It is assumed that there exists a function ψ in D_T which coincides with the boundary conditions $\theta_o(x,t)$ on S_T and $\bar{B}$ at $t = 0$. The initial concentration of reactant is written as $\lambda_o(x,0)$.

Firstly it is intended to show that, provided there does exist a solution of the system (1) and (2) with these boundary and initial conditions, then it is unique.

2.2 Uniqueness of the Solution

This will be approached in the usual way of assuming the existence of two solutions θ_1, λ_1 and θ_2, λ_2 and showing that these are the same.

Theorem 1. Suppose

(a) $\theta_1, \lambda_1, \theta_2, \lambda_2$ exist and are continuous in $\bar{D}_T$,

(b) their second order x_i-derivatives and first order t-derivatives exist and are uniformly bounded in D_T,

(c) $L(\theta_i) = f(x,t,\theta_i,\lambda_i)$,

$$\frac{\partial \lambda_i}{\partial t} = g(x,t,\theta_i,\lambda_i),$$

$\theta_i = \theta_o(x,t)$ on S_T and on $\bar{B}$ at $t = 0$,

$\lambda_i = \lambda_o(x,0)$ on $\bar{B}$ at $t = 0$,

for $i = 1,2$.

(d) f and g satisfy a Lipschitz condition as in equation (12); then $\theta_1 \equiv \theta_2$ and $\lambda_1 \equiv \lambda_2$.

<u>Proof</u>: Define $\theta_r \equiv \theta_1 + re^{mt}$ and $\lambda_s \equiv \lambda_1 + se^{mt}$ where r,s are arbitrary constants and m is some number greater than 2M. (M is the Lipschitz constant defined by (12)). Then since $\theta_1 = \theta_2$ and $\lambda_1 = \lambda_2$ when $t = 0$, unless θ_1 and θ_2, λ_1 and λ_2 coincide for $t > 0$, θ_2 and λ_2 must intersect some members of the family of surfaces θ_r and λ_s. Hence there exists a t' such that $|\theta_2 - \theta_1| \leq |\theta_r - \theta_1|$, $|\lambda_2 - \lambda_1| \leq |\lambda_s - \lambda_1|$ for $t \leq t'$ and either $\theta_2 = \theta_r$ or $\lambda_2 = \lambda_s$ at (x',t'). In the first case choose $r > 0$ and $|s| = r$. Then at the point (x',t') it can be shown by an argument using a theorem of Paraf and Fejér (as in Bateman[12]), that $L(\theta_2) \leq L(\theta_r)$. This means that $L(\theta_2) \leq L(\theta_1) - rme^{mt'}$. That is,

$$\begin{aligned} L(\theta_2) - f(x',t',\theta_2,\lambda_2) &\leq f(x',t',\theta_1,\lambda_1) - f(x',t',\theta_2,\lambda_2) - rme^{mt'} \\ &\leq M(|\theta_2 - \theta_1| + |\lambda_2 - \lambda_1|) - rme^{mt'} \\ &\leq (M(r + |s|) - rm)e^{mt'} \end{aligned}$$

i.e. $L(\theta_2) - f(x',t',\theta_2,\lambda_2) \leq (2M - m)re^{mt'}$.

Since $m > 2M$ this contradicts the assumption that θ_2,λ_2 are solutions of the equations. In the second case choose $s > 0$ and $|r| = s$. Then at the point (x',t'), since $\lambda_2 \leq \lambda_s$ for $t \leq t'$, $\dfrac{\partial\lambda_2}{\partial t} \geq \dfrac{\partial\lambda_s}{\partial t}$.

That is, $\dfrac{\partial\lambda_2}{\partial t} - mse^{mt'} \geq \dfrac{\partial\lambda_1}{\partial t}$. Hence,

$$\frac{\partial\lambda_1}{\partial t} - g(x',t',\theta_1,\lambda_1) \leq g(x',t',\theta_2,\lambda_2) - g(x',t',\theta_1,\lambda_1) - mse^{mt'}$$

$$\text{i.e.}\quad \frac{\partial\lambda_1}{\partial t} - g(x_1', t', \theta_1, \lambda_1) \leqslant M(|\theta_2 - \theta_1| + |\lambda_2 - \lambda_1|) - mse^{mt'}$$

$$\leqslant (M(|r| + s) - ms)e^{mt'}$$

$$\leqslant (2M - m)se^{mt'}.$$

Again, since $m > 2M$ this contradicts the assumption that θ_1, λ_1 are solutions of the equations. Hence no such t' exists and since the argument can be carried through for sufficiently small r and s, the two sets must coincide. That is $\theta_1 \equiv \theta_2$ and $\lambda_1 \equiv \lambda_2$.

This completes the uniqueness theorem under the conditions as stated. It should be noted that the requirement (d), viz. that f and g satisfy a Lipschitz condition in θ and λ, excludes the case of a reaction of order n where $0 \leqslant n < 1$. In this case the functions will not satisfy the Lipschitz condition as $\lambda \to 0$. For example,

$$f = g \equiv \lambda^{\frac{1}{2}}\theta .$$

However in such cases, this difficulty is resolved by redefining f and g in the neighbourhood of $\lambda = 0$, say for $\lambda < \varepsilon$, so that they do in fact satisfy a Lipschitz condition in θ and λ everywhere. Then call the corresponding solutions θ_ε and λ_ε (which by the above will be unique) and define θ and λ as the limits as $\varepsilon \to 0$. It has to be shown, of course, that these limits satisfy the differential equations and, in fact, that they exist. This will be shown in section 2.4, after the problem of existence has been investigated.

2.3 Existence of the Solution

Before the existence proof can be given, three theorems, which form the basis of the existence proof in this section, are required.

The first two of these are proved in Friedman[13].

Theorem 2. Assume that the lateral boundary S_T of D_T is both of classes C^2 and $C^{2+\alpha}$ $(0<\alpha<1)$, that L satisfies the conditions I and II, and that $\phi(x,t)$ is locally Holder continuous in $\bar{D}_T$. Assume finally, that there exists a function ψ of class $C^{2+\alpha}$ in D_T which coincides with the given boundary conditions $\theta_o(x,t)$ on S_T and on $\bar{B}$ at t=0. Then there exists a solution of the system

$$L(\theta) = \phi(x,t) \quad \text{for} \quad (x,t) \text{ in } D_T,$$

$$\theta = \theta_o(x,t) \quad \text{on } S_T \text{ and on } \bar{B} \text{ at } t = 0.$$

Furthermore, the solution is of class $C^{1+\beta}$ in D_T for any $0<\beta<1$ and of class $C^{2+\gamma}$ in $\bar{D}_T$ for some $\gamma>0$.

Theorem 3. Assume that S_T belongs to both C^2 and $C^{2+\alpha}$ and that L satisfies both I and II. Let $\phi(x,t)$ be a continuous function in $\bar{D}_T$ and let $\theta(x,t)$ be a solution of the system

$$L(\theta) = \phi(x,t) \quad \text{in} \quad D_T,$$

$$\theta = \psi \quad \text{on } S_T \text{ and on } \bar{B} \text{ at } t = 0.$$

Then for any $0 \leqq \delta < 1$, there exists a constant P depending only on δ, the operator L, and the domain D_T such that

$$|\theta|_{1+\delta} \leqq P(|\phi|_o + |\psi|_2).$$

Using these two results it is possible to prove the existence of solutions to

$$L(\theta) = \eta(x,t,\theta) \qquad \ldots . (2.14)$$

with the same boundary conditions. In addition to the requirements implied from Theorems 2 and 3, the function η is required to satisfy a Lipschitz condition in θ, i.e.

$$|\eta(x,t,\theta_1) - \eta(x,t,\theta_2)| \leq M|\theta_1 - \theta_2| \quad \text{for all } (x,t) \text{ in } \bar{D}_T.$$

And further it is assumed that there exists two functions $\underline{\theta}$ and $\bar{\theta}$ which are continuous in $\bar{D}_T$, and satisfy the inequalities

$$L(\underline{\theta}) - \eta(x,t,\underline{\theta}) \geqslant 0 \geqslant L(\bar{\theta}) - \eta(x,t,\bar{\theta}), \qquad \text{. . . . (2.15)}$$

$$\underline{\theta}(x,t) \leq \theta_o(x,t) \leqslant \bar{\theta}(x,t) \quad \text{on } S_T \text{ and on } \bar{B} \text{ at } t=0.$$

The proof given in Appendix 1 uses the method of successive approximations. The solution is shown to be of class $C^{1+\beta}$ for any $0 < \beta < 1$ and of class $C^{2+\gamma}$ for some $\gamma > 0$.

The third of the theorems necessary to prove the existence for the system, involves the rate equation (2). That is the existence of a solution to the system

$$\frac{\partial\lambda}{\partial t} = \xi(x,t,\lambda),$$
$$\lambda = \lambda_o(x,0) \quad \text{on } \bar{B} \text{ at } t=0,$$

is required under certain conditions to be prescribed. Note that x is merely a parameter as far as this system is concerned. The statement given here is due to Coddington and Levinson[14].

<u>Theorem 4</u>. Assume ξ is continuous in t and λ. Then there exists a solution of the system

$$\frac{\partial\lambda}{\partial t} = \xi(x,t,\lambda),$$
$$\lambda = \lambda_o(x,0) \quad \text{on } \bar{B} \text{ at } t=0,$$

on some t interval; such that

$$|\lambda(x,t_1) - \lambda(x,t_2)| \leqslant K|t_1 - t_2|.$$

No mention is made of the behaviour of the solution with x. This is given in the following result:-

<u>Corollary</u>. If $\lambda(x,t)$ is a solution to the system in Theorem 4, then,

providing ξ is of class C^1 in x and λ (i.e. satisfies a Lipschitz condition) and $\lambda_o(x,0)$ is of class C^1 in x, λ is also of class C^1 in x. Further λ is bounded in the domain.

Proof: From Theorem 4, taking the solution at any two points x and x', it can be seen that

$$\frac{\partial \lambda(x,t)}{\partial t} = \xi(x,t,\lambda(x,t)),$$

$$\frac{\partial \lambda(x',t)}{\partial t} = \xi(x',t,\lambda(x',t)).$$

Define $h(t) \equiv \lambda(x,t) - \lambda(x',t)$. Then from above

$$\left|\frac{\partial h}{\partial t}\right| = |\xi(x,t,\lambda(x,t)) - \xi(x',t,\lambda(x',t))|,$$

i.e. $\left|\frac{\partial h}{\partial t}\right| \leqslant M_1|x - x'| + M|h|$

where M_1 and M are the Lipschitz constants for $\xi(x,t,\lambda)$. Then by considering $h \lesseqgtr 0$ separately and integrating the last result, it can be shown that $|h| \leqslant M'|x - x'|$. That is, $|\lambda(x,t) - \lambda(x',t)| \leqslant M'|x - x'|$, for any x,x'; which is the required result. The second result is obtained from taking the Lipschitz condition for ξ,

$|\xi(x,t,\lambda) - A| \leqslant M|\lambda|$, where $A = \xi(x,t,0)$. Hence,

$\left|\frac{\partial \lambda}{\partial t}\right| \leqslant |A| + M|\lambda|$. Again, by considering $\lambda \lesseqgtr 0$ separately and integrating, upper and lower bounds are obtained for λ.

It is now possible to prove the main result of this section. The proof which is given in Appendix 2 was motivated by the remarks made earlier in this chapter. An iterative scheme is set up and it is shown that the sequences so obtained converge to the solutions of the system given in (1) and (2). A fundamental step in establishing the result is a theorem proved by Ascoli which (as in Coddington and Levinson) is stated here as a lemma. This result enables us to say that there exists a limit to the sequences so obtained.

Ascoli's Lemma. On a bounded domain D, let $\Theta = \{\theta\}$ be an infinite, uniformly bounded, equicontinuous set of functions. Then Θ contains a sequence $\{\theta_n\}$, n = 1,2,.., which is uniformly convergent on D.

One restriction that has been applied, a physical one taken from the real problem, is that the reactant concentration is confined between its initial concentration and zero. All this is saying is that the reactant is being consumed as time proceeds and can only be consumed as long as the concentration is greater than zero. Hence g will be negative, and zero when λ is zero. This requirement can be relaxed though it means a further difficulty with obtaining uniform bounds for the iterative solutions for λ_n. This is however, simple to resolve, though this is not done in the proof given in Appendix 2.

2.4 The Cut-off Problem

It will be shown later that for a reaction of order less than unity, the reactant will be exhausted in a finite time. For such reactions it is clear from the examples given previously, that the functions f and g will not satisfy the Lipschitz condition in the neighbourhood of $\lambda = 0$. So it is necessary to show that there exists a unique solution when this condition is relaxed i. e. when the reaction is of order less than unity. In a reaction of zero order both f and g will be discontinuous on $\lambda = 0$. It will be shown that λ is of class C^1 as before, but θ will not be of class $C^{2+\alpha}$ uniformly in $\bar{D}_T$. The reason for this limitation is the discontinuity in f on $\lambda = 0$ only.

It will be assumed here that heat is being liberated only, that is the reaction is exothermic. The physical situation from which this analysis arose did in fact ensure this, but the results in the previous sections can be applied to endothermic reactions also.

The problem will be approached by redefining the function f for $\lambda \leqslant \varepsilon$ as follows:

$$f_\varepsilon(x,t,\theta,\lambda) \begin{array}{ll} = f(x,t,\theta,\lambda), & \lambda > \varepsilon \\ = \dfrac{2\lambda^2}{\varepsilon^3}(3\varepsilon/2 - \lambda)f(x,t,\theta,\lambda), & 0 \leqslant \lambda \leqslant \varepsilon \\ = \quad 0 \;, & \lambda < 0 \end{array}$$

where ε is small. The variation of f_ε with λ for any fixed (x,t) in $\bar{D}_T$ and any value of θ is compared with that of f in Fig. 2.1.

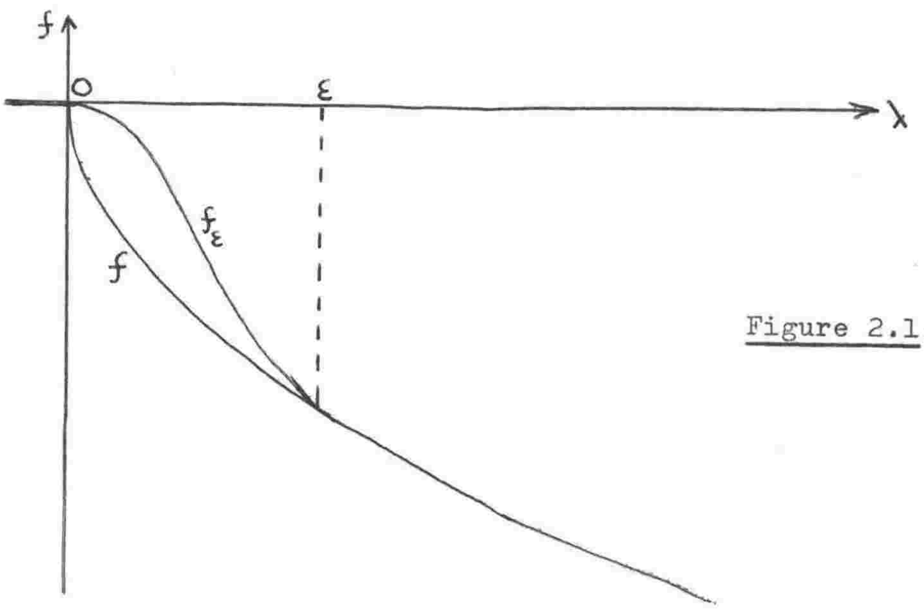


Figure 2.1.

Then with the assumptions of the previous theorems, define

$$\frac{\partial \lambda_1}{\partial t} = g(x,t,\bar{\theta},\lambda_1) ,$$

$$L(\theta_n) = f_{\varepsilon_n}(x,t,\theta_n,\lambda_n), \qquad n \geqslant 1$$

$$\frac{\partial \lambda_n}{\partial t} = g(x,t,\theta_{n-1},\lambda_n), \qquad n = 2,3,\ldots$$

with $\theta_n = \theta_0(x,t)$ $n \geqslant 1$, on S_T and on $\bar{B}$ at $t = 0$, and $\lambda_n = \lambda_0(x,0)$ $n \geqslant 1$, on $\bar{B}$ at $t = 0$. Further (ε_n) is a monotone decreasing sequence of positive numbers such that $(\varepsilon_n) \to 0$ as $n \to \infty$. For each n, there exists a $\theta_n(x,t)$ and $\lambda_n(x,t)$ in $\bar{D}_T$ such that θ_n is of class $C^{2+\gamma}$ $(\gamma > 0)$ in $\bar{D}_T$ and $\lambda_n(x,t)$ is continuous in $\bar{D}_T$. Since heat is being liberated only it follows that $\theta_n \geqslant \theta_0$ and hence θ_0 will serve as a lower bound. Further, since from the main result (in Appendix 2) it was assumed that there exists a $\bar{\theta}(x,t)$ such that

$$0 \geqslant L(\bar{\theta}) - f(x,t,\bar{\theta},\lambda) \quad \text{for a prescribed range of } \lambda,$$

$$\bar{\theta} \geqslant \theta_0 \quad \text{on the boundaries of } D_T,$$

and as $\quad f_\varepsilon \geqslant f,$

it follows that $\theta_n \leqslant \bar{\theta}$ in $\bar{D}_T$. That is the same $\bar{\theta}$ serves as an upper bound for the sequence of functions (θ_n). From the estimates of Friedman given in Theorem 3, it also follows that

$$|\theta_n|_{1+\delta} \leqslant P(|f(x,t,\theta_n,\lambda_n)|_0 + |\psi|_2).$$

As both the θ_n's and λ_n's are bounded in $\bar{D}_T$ $(\theta_0 \leqslant \theta_n \leqslant \bar{\theta},\ 0 \leqslant \lambda_n \leqslant \lambda_0)$, then θ_n and $\partial\theta_n/\partial x_i$ are Hölder continuous of exponent δ for all i. This means that the set of functions (θ_n) are equicontinuous on $\bar{D}_T$ and so, by Ascoli's lemma, there exists a limit θ defined on $\bar{D}_T$ which is Holder continuous of exponent δ in $\bar{D}_T$. This follows exactly as in the previous existence theorem. Similarly $\partial\theta/\partial x_i$ is Hölder continuous of exponent δ in $\overline{D}_T$. These estimates will apply for all types of reactions i.e. for any reaction order. It will be shown below that in all reactions other than one special case, the estimates can be improved.

However, first some properties must be established for the function λ_n. From the equation

$$\frac{\partial\lambda_n}{\partial t} = g(x,t,\theta_{n-1},\lambda_n),$$

write

$$g = \lambda^\alpha h(x,t,\theta,\lambda), \quad (0 \leq \alpha < 1), \quad \lambda > 0$$

where h is of class C^1, and

$$g = 0 \qquad \text{when} \quad \lambda = 0.$$

Then if $\mu^\beta = \lambda$, where $\beta = 1/(1-\alpha)$ it follows that

$$\frac{\partial\mu_n}{\partial t} = \frac{1}{\beta}h(x,t,\theta_{n-1},\mu_n{}^\beta), \quad (\beta \geqslant 1) \text{ and } \mu_n > 0,$$

$$\frac{\partial\mu_n}{\partial t} = 0 \qquad \text{for } \mu_n = 0.$$

Clearly $\mu_n(x,t)$ will be uniformly of class C^1 in each region and so μ_n is of class C^1 in the whole region $\overline{D}_T$. This follows since μ_n is continuous on the common boundary of the separate regions $\mu_n > 0$ and $\mu_n = 0$. Hence

$$|\mu_n(P) - \mu_n(Q)| \leq M|P-Q| \quad \text{for any } P,Q \in \overline{D}_T$$

where $|P-Q| = |x-x'| + |t-t'|$ if $P = (x,t)$, $Q = (x',t')$. From this it is possible to deduce that λ_n is of class C^1 in $\overline{D}_T$ as follows. Consider

$$\frac{|\lambda_n(P)-\lambda_n(Q)|}{|P-Q|} = \frac{|\mu_n{}^\beta(P)-\mu_n{}^\beta(Q)|}{|\mu_n(P)-\mu_n(Q)|} \cdot \frac{|\mu_n(P)-\mu_n(Q)|}{|P-Q|},$$

and note that the second factor is uniformly bounded in $\overline{D}_T$. Also since the μ_n 's are bounded on $\bar{D}_T$ $(0 \leq \mu_n \leq [\lambda_o(x,0)]^\beta)$, and by noting the following lemma it follows that the first factor is bounded on $\bar{D}_T$.

Lemma: There exists a upper bound for $\frac{|a^\beta - b^\beta|}{|a-b|}$ for $0 \leq a,b \leq R$, $\beta \geq 1$.

Proof: Suppose $a \geq b$. Then the expression can be written

$$\frac{(a^\beta - b^\beta)}{a-b} = \frac{a^{\beta-1}(1-(b/a)^\beta)}{(1-b/a)} \leq a^{\beta-1} \leq R^{\beta-1} .$$

So λ_n is of class C^1 in $\bar{D}_T$. Thus the set of functions (λ_n) are therefore equicontinuous on $\bar{D}_T$ and so, once more by Ascoli's lemma, there exists a limit λ defined on $\bar{D}_T$. Likewise there exists a limit μ which is the limit of the sequence of functions (μ_n) and $\mu^\beta = \lambda$. As in Appendix 2 it is possible to prove μ is of class C^1 in $\bar{D}_T$ from the equations satisfied by each μ_n. Then, from an argument as above, it follows that λ is also of class C^1 in $\bar{D}_T$.

The quantities θ and λ of class C^1 is sufficient to ensure the existence of a solution to

$$\frac{\partial \lambda'}{\partial t} = g(x,t,\theta,\lambda),$$

$$\lambda' = \lambda_o(x,0) \quad \text{on } \bar{B} \text{ at } t = 0,$$

with the interpretation that $g = 0$ when $\lambda = 0$. λ' is of class C^1 in $\bar{D}_T$. Now

$$\frac{\partial}{\partial t}(\lambda' - \lambda_n) = g(x,t,\theta,\lambda) - g(x,t,\theta_{n-1},\lambda_n) ,$$

and $\lambda' - \lambda_n = 0$ on $\bar{B}$ at $t = 0$.

i.e. $\frac{\partial}{\partial t}(\lambda' - \lambda_n) \leq M(|\theta - \theta_{n-1}| + |\lambda - \lambda_n|)$ where the right hand side tends to zero as n tends to infinity. Thus λ' coincides with λ in $\overline{D}_T$. And so $\partial\lambda/\partial t$ exists also.

It can be shown that the surface defined by $\lambda_n(x,t)=0$, i.e. $t=C_n(x)$, tends to that of $\lambda(x,t)=0$, i.e. $t=C(x)$, uniformly in $\overline{B}$ as n tends to infinity. Consider, as before,

$$\frac{\partial\mu_n}{\partial t} = \frac{1}{\beta}h(x,t,\theta_{n-1},\mu_n{}^{\beta}),$$

$$\frac{\partial\mu}{\partial t} = \frac{1}{\beta}h(x,t,\theta,\mu^{\beta}).$$

Then by definition of μ , it follows that $\mu_n(x,t) \longrightarrow \mu(x,t)$, $\partial\mu_n/\partial t \rightarrow \partial\mu/\partial t$ uniformly in $\overline{D}_T$ as n tends to infinity. Note that the cut-off surface given by $\mu(x,t)= 0$ is that of $t= C(x)$. Then $\mu_n(x,C(x)) \rightarrow \mu(x,C(x))$ as n tends. Now the function h can be taken as independent of μ for $t < C(x)$. Hence, $\partial\mu_n/\partial t$ is less than $-a$ for all n, where $a > 0$.

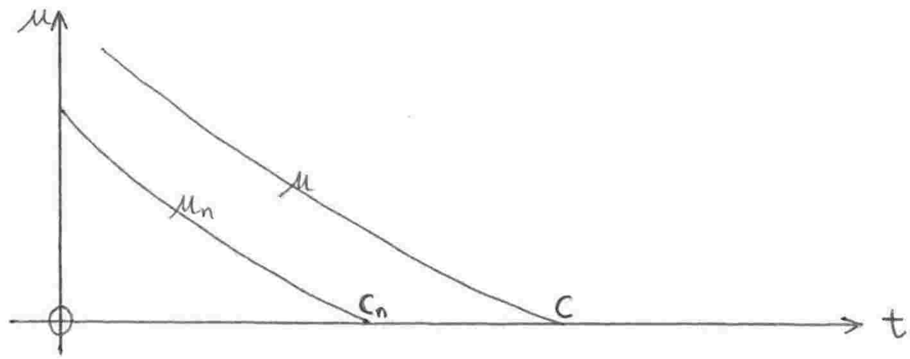


Fig. 2.2

Consider,(i) $C_n \leqslant C$. Then $\dfrac{\mu(x,C_n) - \mu(x,C)}{C_n - C} \leqslant -a$,

i.e. $\mu(x,C_n) - \mu(x,C) \geqslant a(C - C_n)$. And so as the right hand side tends to zero as n tends, so $C_n \rightarrow C$ as $n \rightarrow \infty$.

(ii) $C_n \geqslant C$. The argument follows as above, with μ_n and μ interchanged. Hence it can be concluded that $C_n(x) \rightarrow C(x)$ as $n \rightarrow \infty$, uniformly in $\bar{B}$.

Also, by considering

$$\frac{\partial h}{\partial t} = g(x,t,\theta(x,t),\lambda(x,t)) - g(x',t,\theta(x',t),\lambda(x',t)),$$

where $h(t) = \lambda(x,t) - \lambda(x',t)$, it is possible to show that the surface $C(x)$ is of class C^1 in x, uniformly in $\bar{B}$. This means that $\partial C/\partial x_i$ is finite everywhere for all i.

Now, excluding the case in which $\lim_{n\to\infty} f_{\epsilon_n}(x,t,\theta,\lambda)$ is discontinuous at $\lambda = 0$, it can be shown that θ and λ satisfy the system (1) and (2). It has already been shown that λ does satisfy the equations and the same result follows for θ. This means that θ is of class $C^{1+\beta}$ in D_T for any $0<\beta<1$ and of class $C^{2+\gamma}$ in $\bar{D}_T$ for some $\gamma > 0$. In particular, this means that the temperature θ, its first two derivatives in x_i, and its first derivative in t, are continuous on the surface $t = C(x)$.

However, in the case where f is discontinuous on $\lambda = 0$ (this coincides with the idea of a zero-order reaction but the discontinuity in g does not affect the analysis), the two regions $\lambda > 0$ and $\lambda = 0$ are considered independently. In fact the problem is considered as two separate problems which both have solutions by the results of section 3:

I. $L(\theta) = f(x,t,\theta,\lambda)$,

$$\frac{\partial\lambda}{\partial t} = g(x,t,\theta,\lambda),$$

$\theta = \theta_0(x,t)$ on S_T and on $\bar{B}$ at $t = 0$.

$\lambda = \lambda_0(x,0)$ on $\bar{B}$ at $t = 0$,

in the closure of the region

$$E = \{(x,t): x \in B, (x,t) \in D_T, t < C(x)\}.$$

II. $\quad L(\theta) = f(x,t,\theta,0),$

$$\theta = \theta_o(x,t) \text{ on } S_T$$

in the closure of the region

$$F = \{(x,t): x \in B, (x,t) \in D_T, t > C(x)\}.$$

It is assumed that the boundaries of these regions satisfy the conditions required by Friedman in Theorems 2 and 3. That is, they are both of classes C^2 and $C^{2+\alpha}$ for some $\alpha > 0$. If this is not so, then remove a strip about $t = C(x)$ so that the boundaries of E and F do satisfy this condition. These theorems imply that θ is of class $C^{2+\gamma}$ for some $\gamma > 0$ in each of $\bar{E}$ and $\bar{F}$. Note that in order to solve II use is made of the estimate obtained early in this section, that is the $1+\delta$ estimate. This means that θ and $\partial\theta/\partial x_i$, for all i, are continuous on $t = C(x)$, and this will be all the information that can be obtained for this particular type of reaction. By considering the equation for σ, equation (1), it can be seen why no information is gained for $\partial\theta/\partial t$. In the special case $C(x)$ is a constant, i.e. $t = C(x)$, and this will be a characteristic of the equation $L(\theta) = f$, it follows that the second derivatives of θ with respect to x_i are continuous and $\partial\theta/\partial t$ will have a finite discontinuity on $t = C(x)$. The precise value of this discontinuity will be in fact the value of the heat source just prior to the complete exhaustion of the reactant. However, in the general case it is not possible to attribute the discontinuity on $t = C(x)$ wholly to either of $\partial\theta/\partial t$ or to the second derivatives of θ with respect to the x_i. This concludes the discussion of the cut off problem.

Chapter 3

COMPARISON RESULTS AND THEIR APPLICATION TO SPECIAL PROBLEMS

Many existence proofs of systems such as those discussed in this thesis, begin by establishing a comparison theorem which enables bounds to be obtained for the iterations set up. McNabb[10] took this approach in proving the existence and uniqueness of the system (2.1) and (2.2), when f is a nonincreasing function of λ and g is a nondecreasing function of θ. His preliminary result was used in Chapter 2 to establish the existence and uniqueness of the system therein defined. The result proved by McNabb is stated here as the following theorem.

Theorem 5. Suppose,

(a) θ_1, θ_2, λ_1, λ_2 exist and are continuous in $\overline{D}_T$.

(b) Their second order x_i-derivatives and first order t-derivatives exist and are uniformly bounded in D_T, satisfying there the inequalities

$$L(\theta_1) - f(x,t,\theta_1, \lambda_1) \geqslant L(\theta_2) - f(x,t,\theta_2, \lambda_2),$$

$$\frac{\partial\lambda_1}{\partial t} - g(x,t,\theta_1, \lambda_1) \leqslant \frac{\partial\lambda_2}{\partial t} - g(x,t,\theta_2, \lambda_2),$$

and where,

$$\partial f/\partial\lambda \leqslant 0, \ \partial g/\partial\theta \geqslant 0.$$

(c) $\theta_1 \leqslant \theta_2$ on S_T and $\theta_1 \leqslant \theta_2$, $\lambda_1 \leqslant \lambda_2$ on $\overline{B}$ at $t=0$.

Then $\theta_1 \leqslant \theta_2$ and $\lambda_1 \leqslant \lambda_2$ in $\overline{D}_T$.

Zeragija[11] likewise attempted to establish a similar result for the system he described (see Chapter 2).

In this chapter it will be shown that it is not possible to establish a comparison theorem in the general case without invoking requirements on the boundary conditions. This will be followed by some examples in which it is possible to obtain upper and lower bounds on the solution.

3.1. Counter-example

In this section an example will be given to illustrate the statement that a general comparison theorem is impossible. This will be done by considering the system (2.1) and (2.2), with, at present, no requirements on the functions f and g.

It will be assumed that:

$$f = a\theta + b\lambda,$$

$$g = a\theta + b\lambda,$$

where a and b are constants. For simplicity, the geometry shall be confined to $q = 1$ and $|x| < \pi/2$. Thus the equations are

$$\frac{\partial^2\theta}{\partial x^2} - \frac{\partial\theta}{\partial t} = a\theta + b\lambda, \qquad \ldots . (3.1)$$

$$\frac{\partial\lambda}{\partial t} = a\theta + b\lambda. \qquad \ldots . (3.2)$$

This problem will be posed with zero boundary and initial values. Hence the solution of the above will be the trivial solution:

$$\theta = 0, \ \lambda = 0. \qquad \ldots . (3.3)$$

This solution will be the known solution for which comparison functions will be found. These will be obtained simply by separating the variables. It will be shown that in general it is impossible to find functions p,q which remain of constant sign for all t, i.e. which are consistent upper and lower bounds for the solution (3).

If one proceeds in the way indicated by Theorem 5, and attempts to find solutions θ', λ' which satisfy

$$\frac{\partial^2\theta'}{\partial x^2} - \frac{\partial\theta'}{\partial t} \leqslant a\theta' + b\lambda',$$

$$\frac{\partial\lambda'}{\partial t} \geqslant a\theta' + b\lambda',$$

it would be expected that, provided the initial and boundary conditions are specified correctly, θ', λ' are upper bounds for the solutions to equations (1) and (2). Note that Theorem 5 applies only to the case $a \geqslant 0$, $b \leqslant 0$. In the above the case of equality will be taken. Further, take the boundary condition for θ' as $\theta' = 0$ on $x = \pm\pi/2$,

and try

$$\theta' = p(t)\cos x, \qquad \ldots . (3.4)$$

$$\lambda' = q(t)\cos x, \qquad \ldots . (3.5)$$

as a solution of the problem. Hence, on substitution in the equations, it follows that p,q must satisfy

$$\dot{p} = -(a+1)p - bq, \qquad \ldots . (3.6)$$

$$\dot{q} = ap + bq, \qquad \ldots . (3.7)$$

where $\dot{} \equiv \frac{d}{dt}$. These two equations are to be solved with the initial conditions: $p(0) = P$, $q(0) = Q$.

Both p and q are thus solutions of the second order equation

$$\ddot{r} + (a+1-b)\dot{r} - br = 0, \qquad \ldots . (3.8)$$

the solutions of which are $e^{\alpha t}$ where α satisfies

$$\alpha^2 + (a+1-b)\alpha - b = 0. \qquad \ldots . (3.9)$$

From (6) and (7) it follows that

$$\frac{dp}{dq} = \frac{-(a+1)p - bq}{ap + bq} \qquad \ldots . (3.10)$$

Try a solution of the form $p = kq$. This means that

$$ak^2 + (a+1+b)k + b = 0, \qquad \ldots . (3.11)$$

the discriminant of which is given by $(1+a+b)^2 - 4ab$; the same as that of equation (9). Call these roots k_1, k_2. By considering the p,q plane it can be seen that the solution must lie between these lines. For $p = k_1q$, $p = k_2q$ are two possible solutions and no solution can cross another at a regular point. It will be assumed that k_2 is the greater of these (whenever the discriminant is positive). This area is shown in Fig. 3.1.

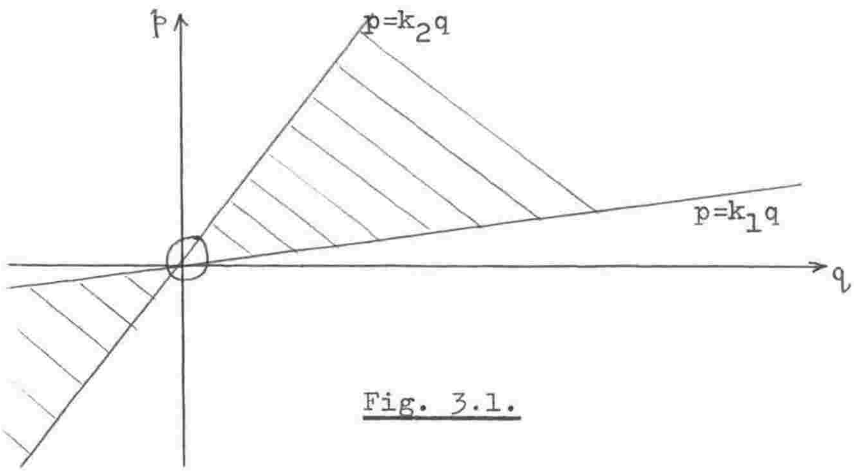


Fig. 3.1.

Further, if the tangent to the solution at a point passed through the origin, then at this point it follows that

$$k = \frac{-(a+1)k - b}{ak + b}, \qquad \text{i.e. } k = k_1 \text{ or } k_2.$$

Thus the only possible tangents to the solution passing through the origin are the lines $p = k_1q$, $p = k_2q$.

Now since the discriminants of equations (8) and (11) are the same, then the case in which k_1 and k_2 are real coincides with the condition that p,q vary as $e^{\alpha t}$ where α is real. So one obvious requirement for p and q to be of the same sign for all t is that this discriminant is positive. That is,

$$(a+b+1)^2 - 4ab \geqslant 0. \qquad \qquad . . . . (3.12)$$

For if this were not so, the solutions for p,q would oscillate about the origin in spirals or ellipses (c.f. Stoker[15]).

For t small, p,q varies like $e^{k_1 t}$, and for t large they vary like $e^{k_2 t}$. Whether or not k_1 and k_2 are of the same sign depends on the sign of b/a. To ascertain the form of the integral curves the various cases are considered. In each case arrows are drawn along the integral curve to indicate the direction of t increasing. Also it is assumed in all cases that the requirement (12) is satisfied. From Stoker, the form of the singularity is either a nodal point or a saddle point depending solely on the sign of the determinant formed from equations (6) and (7). That is whether or not $-ab + (a+1)b = b \lesseqgtr 0$.

I. $a \geqslant 0$, $b \leqslant 0$ (the case covered by Theorem 5).

Here $k_1 k_2 \leqslant 0$ and so $k_2 \geqslant 0$, $k_1 \leqslant 0$. From the criteria of Stoker, the singularity is a nodal point. See Fig. 3.2 overleaf.

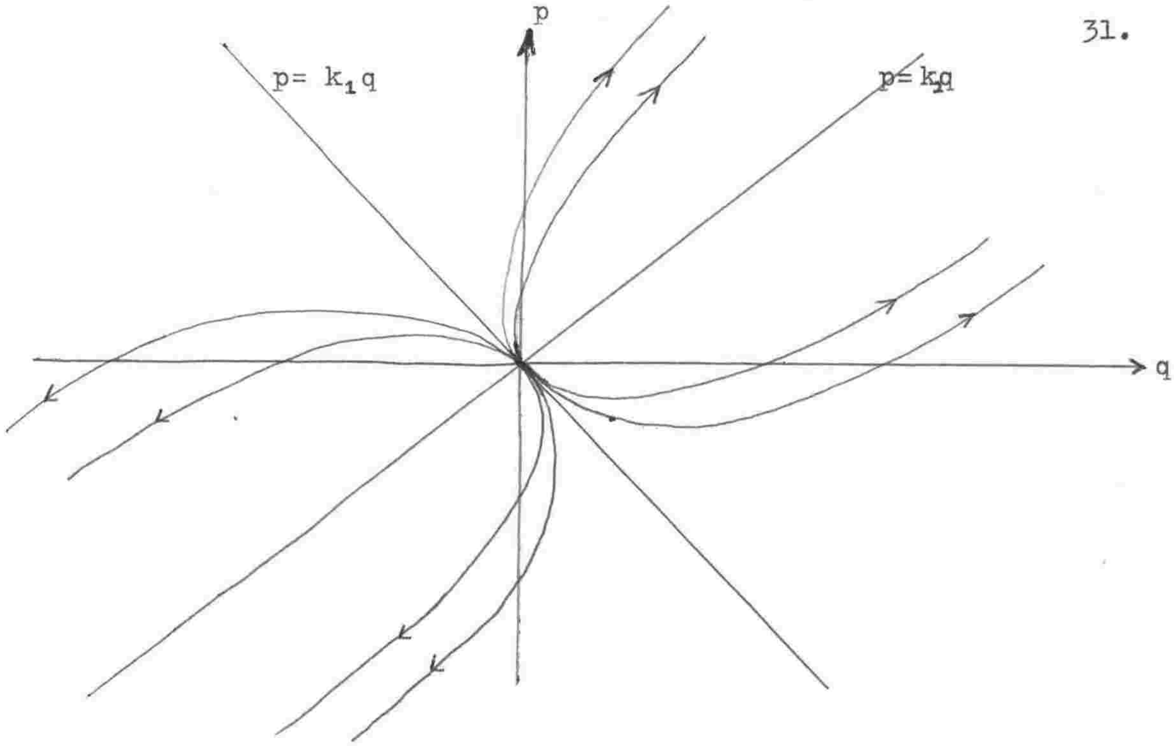


Fig. 3.2

II. $a \leq 0$, $b \geq 0$.

Again $k_2 \geq 0$, $k_1 \leq 0$, but this time the singularity is a saddle point. See Fig. 3.3.

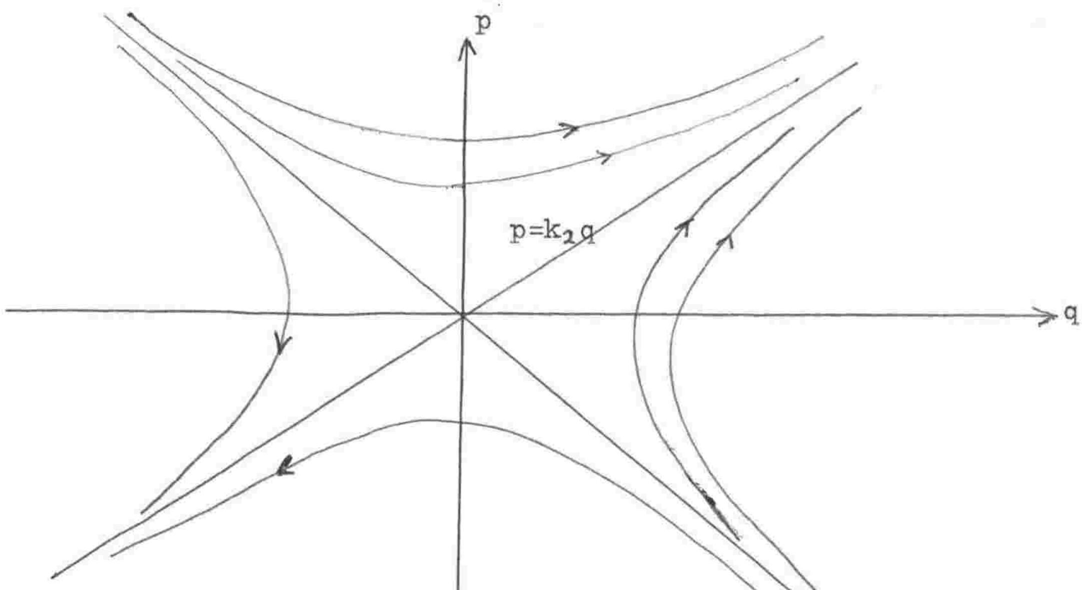


Fig. 3.3

Now in cases I and II, if the initial values (Q,P) are such that $P/Q \geqslant 0$, then clearly for $t > 0$ the solution remains in the same quadrant and so p and q remain of the same sign. This means that a comparison theorem is possible. (Note that since $ab \leqslant 0$, condition (12) is always satisfied).

III. $a \geqslant 0$, $b \geqslant 0$, such that (12) is satisfied.

Hence k_1, k_2 are of the same sign and the singularity is a saddle point.

(i) k_1, k_2 both positive:

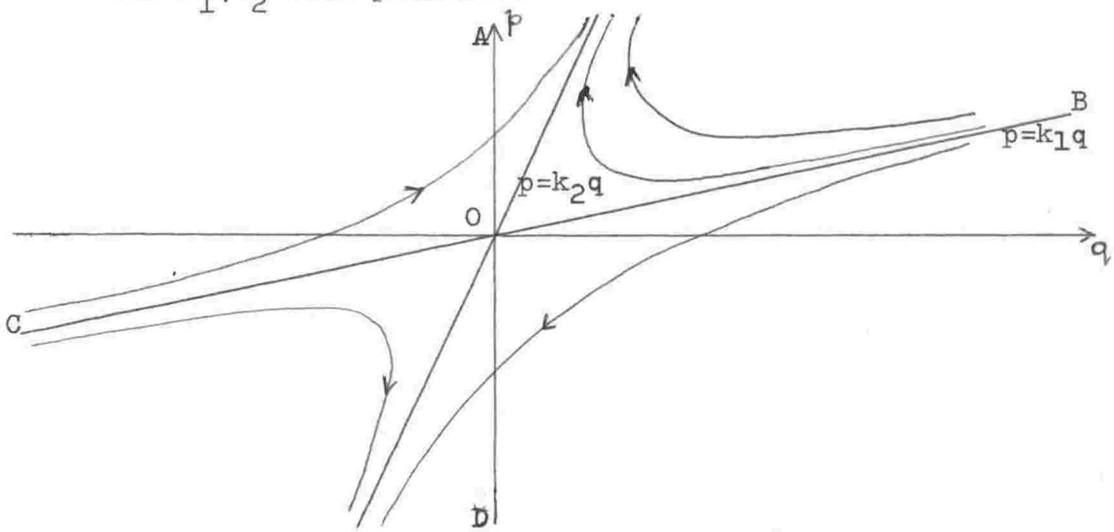


Fig. 3.4

(ii) k_1, k_2 both negative:

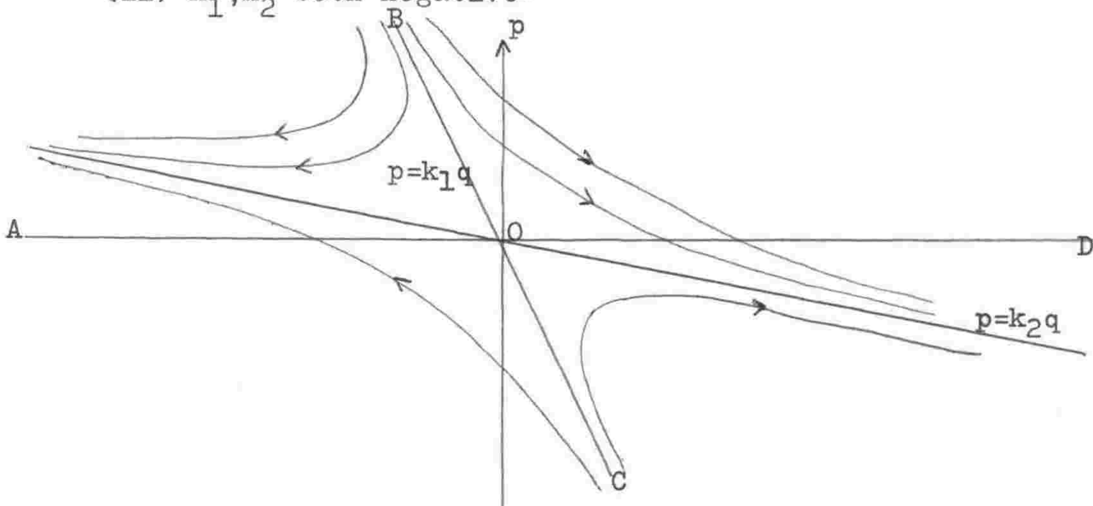


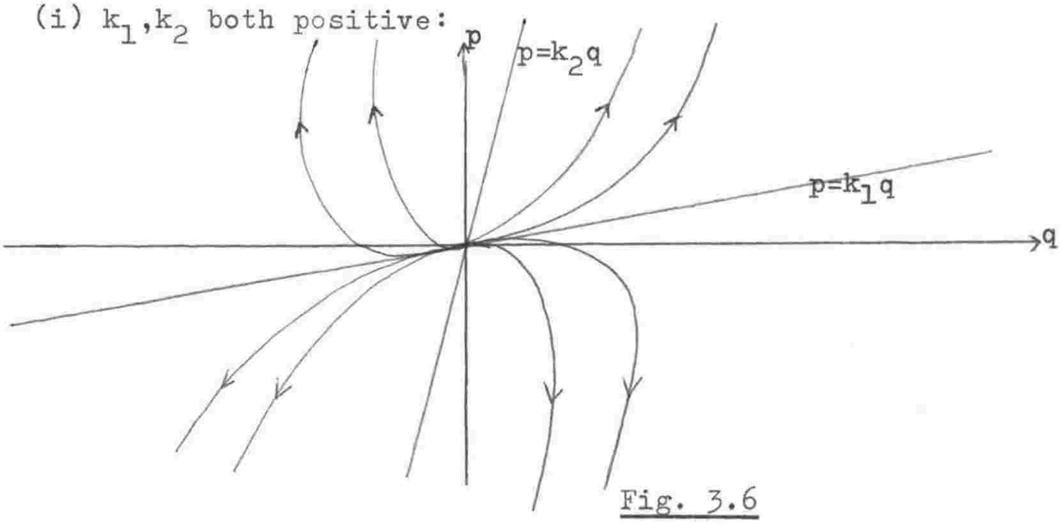
Fig. 3.5

Then it is clear that for each of p,q to remain of the same sign, the initial values must satisfy $k_1 \leq P/Q$ in the first case, and $0 \geqslant P/Q \geqslant k_1$ in the second case. That is (Q,P) is in the region AOB or DOC in (i), and also in (ii). This means that a comparison theorem is <u>impossible</u> without restricting the initial conditions.

IV. $a \leq 0$, $b \leq 0$, such that (12) is satisfied.

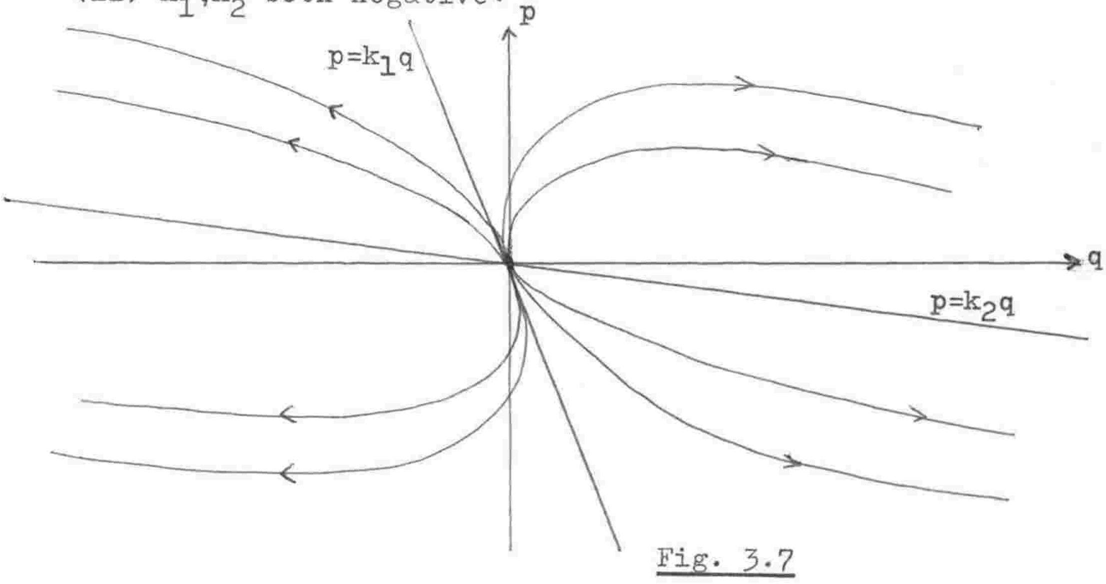
Hence, once more k_1, k_2 are of the same sign, but the singularity is now a nodal point.

(i) k_1, k_2 both positive:



<u>Fig. 3.6</u>

(ii) k_1, k_2 both negative:



<u>Fig. 3.7</u>

In these cases for p,q to remain of the same sign the initial values must satisfy $P/Q \geqslant k_1$ in case (i) and $0 \geqslant P/Q \geqslant k_1$ in case (ii). That is, exactly as in III.
Note that if the discriminant in (12) is zero, the singularity is always a nodal point.

Hence it can be seen that, in general it is impossible to state a comparison theorem applicable to all cases, without some extra conditions. Most of the examples discussed later are reactions in which f is nonincreasing in λ ($b \not> 0$) and g is nonincreasing in σ ($a \not> 0$). That is, case III.

3.2. Bounds for the Solutions.

Following the remarks made early in Chapter 2, that is, by taking upper and lower bounds for λ, upper and lower bounds are obtained for θ. In view of the comments in the previous section, however, no direct comparison theorem is possible. Hence to obtain upper and lower estimates for θ an equation of the form

$$\Delta\theta' - \frac{\partial\theta'}{\partial t} = f(x,t,\theta',\lambda'), \qquad \ldots . (3.13)$$

is solved. If f is nonincreasing in λ, it follows that if λ' is an upper (lower) bound for λ then θ' is an upper (lower) bound for θ. Similarly, estimates can be obtained for λ by using upper and lower bounds for θ.

However, it is possible for a certain class of reactions to uncouple the differential equations and so get a solution of the form

$$\Delta\phi + f(\phi) = \frac{\partial\phi}{\partial t}. \qquad \ldots . (3.14)$$

It will be shown that, by considering the solutions of (14) and bounds for these solutions, bounds can be obtained for the reactant concentration (λ).

Consider the system

$$\frac{\partial^2\theta}{\partial x^2} + a\lambda^n\theta = \frac{\partial\theta}{\partial t}, \qquad \ldots . \ (3.15)$$

$$\frac{\partial\lambda}{\partial t} = -\lambda^n\theta \qquad \ldots . \ (3.16)$$

in the semi-infinite region x 0 where $\theta = \lambda = 1$ when $t = 0$ and $x > 0$
$\theta = 1$ on $x = 0$. a is a constant and $n \neq 1$. Equation (16) can thus be written

$$\frac{\partial}{\partial t}\left(\frac{\lambda^{1-n}}{n-1}\right) = \theta, \qquad \ldots . \ (3.17)$$

and hence by defining $\phi = \dfrac{\lambda^{1-n}}{n-1}$ i.e. $\theta = \dfrac{\partial\phi}{\partial t}$, it follows that

$$\frac{\partial^2}{\partial x^2}\left(\frac{\partial\phi}{\partial t}\right) + a(n-1)^{n/1-n}\phi^{n/1-n}\frac{\partial\phi}{\partial t} = \frac{\partial^2\phi}{\partial t^2} \qquad \ldots . \ (3.18)$$

On integrating and noting that $\phi = -1/(1-n)$, $\partial\phi/\partial t = 1$ when $t = 0$ equation (18) gives

$$\frac{\partial^2\phi}{\partial x^2} + 1 + a(1-(\overline{n-1}\phi)^{1/(1-n)}) = \frac{\partial\phi}{\partial t}. \qquad \ldots . \ (3.19)$$

This is an equation of the form indicated in (14). When $n = 1$ define $\phi = -\log\lambda$ i.e. $\lambda = e^{-\phi}$. Then as above it follows that

$$\frac{\partial^2\phi}{\partial x^2} + 1 + a(1-e^{-\phi}) = \frac{\partial\phi}{\partial t}, \qquad \ldots . \ (3.20)$$

subject to the boundary and initial conditions,

$$\phi = 0 \text{ when } t = 0,$$

$$\phi = t \quad \text{on} \quad x = 0,$$

$$\frac{\partial\phi}{\partial x} \rightarrow 0 \quad \text{as} \quad x \rightarrow \infty.$$

Again an equation of the form suggested by (14) results.

Now to illustrate the ideas involved, this latter equation will be taken as an example. Use can now be made of Theorem 5 which can be stated:

If ϕ_1, ϕ_2 exist and satisfy

$$\frac{\partial^2\phi_1}{\partial x^2} - \frac{\partial\phi_1}{\partial t} + f(\phi_1) \geqslant \frac{\partial^2\phi_2}{\partial x^2} - \frac{\partial\phi_2}{\partial t} + f(\phi_2) \quad \text{for } x,t > 0,$$

$$\phi_1 \leqslant \phi_2 \qquad \text{on } x = t = 0;$$

$$\text{then } \phi_1 \leqslant \phi_2 \qquad \text{everywhere.}$$

One selects various "comparison functions" and takes either ϕ_1 or ϕ_2 as the required solution. Three of the possibilities are discussed below:

1. The solution independent of x. This will be the asymptotic value of the solution of (20) as x ∞. It can be shown by direct integration of

$$1 + a(1-e^{-\phi}) = \frac{d\phi}{dt},$$

with the initial condition of $\phi = 0$ when $t = 0$, to be

$$\phi_\infty = \log\left(\frac{a + e^{(1+a)t}}{1 + a}\right). \qquad \ldots . \; (3.21)$$

This will be an upper bound. Taking ϕ_2 as that defined in (21) and note that on $x = 0$, $\phi_1 = \phi = t$ and that

$$t \leqslant \log\left(\frac{a + e^{(1+a)t}}{1 + a}\right) \qquad \text{for any } a \geqslant 0.$$

Hence it follows that the solution of (20) satisfies

$$\phi \leqslant \log\left(\frac{a + e^{(1+a)t}}{1 + a}\right) \qquad \text{for all } x,t \geqslant 0. \qquad \ldots \; (3.22)$$

It should be noted at this stage that the solution at infinity for θ and λ satisfying (15) and (16) when n = 1, is given by

$$\theta_{\infty} = \frac{\partial \phi}{\partial t} \quad \text{and} \quad \lambda_{\infty} = e^{-\phi},$$

i.e. $$\theta_{\infty} = \frac{1 + a}{1 + ae^{-(1+a)t}} \quad \text{and} \quad \lambda_{\infty} = \frac{1 + a}{a + e^{(1+a)t}} \qquad . . (3.23)$$

In view of the inequality in (22) it follows that

$$\lambda \geqslant \frac{1 + a}{a + e^{(1+a)t}} \qquad \text{for all } x, t \geqslant 0.$$

2. A lower bound may be constructed by taking $\phi_1 = r(x,t)\phi_{\infty}$, for some suitable function r. If $F(\phi) \equiv \frac{\partial^2 \phi}{\partial x} - \frac{\partial \phi}{\partial t} + 1 + a(1 - e^{-\phi})$, and ϕ_1 is to be a lower bound, then r must be such that $F(\phi_1) \geqslant 0$. Hence it is required that

$$\phi_{\infty}\left(\frac{\partial^2 r}{\partial x} - \frac{\partial r}{\partial t}\right) - r\frac{d\phi_{\infty}}{dt} + 1 + a(1 - e^{-r\phi_{\infty}}) \geqslant 0,$$

i.e. $$\phi_{\infty}\left(\frac{\partial^2 r}{\partial x^2} - \frac{\partial r}{\partial t}\right) + 1 - r + a(1 - r + re^{-\phi_{\infty}} - e^{-r\phi_{\infty}}) \geqslant 0,$$

and also $r \to 1$ as $x \to \infty$. That is, $\phi_1 \to \phi_{\infty}$.

Then take r satisfying

$$\frac{\partial^2 r}{\partial x^2} - \frac{\partial r}{\partial t} = 0,$$

$$r = 0 \quad \text{on } x = 0,$$

$$r = 1 \quad \text{on } t = 0.$$

Therefore $r(x,t) = \operatorname{erf}(x/2t^{\frac{1}{2}})$, and thus $0 \leqslant r \leqslant 1$.

It remains to show that the expression

$$E \equiv 1 - r + re^{-\phi_{\infty}} - e^{-r\phi_{\infty}} \geqslant 0$$

for $\phi_\infty \geqslant 0$ and $0 \leqslant r \leqslant 1$. Consider E as a function of ϕ_∞ and r.

$$\frac{\partial E}{\partial \phi_\infty} = r(e^{-r\phi_\infty} - e^{-\phi_\infty}) \geqslant 0$$

and $E = 0$ on $\phi_\infty = 0$. Therefore $E \geqslant 0$. Thus $F(\phi_1) \geqslant 0$. Also when $t = 0$, $\phi_1 = \phi_2 = 0$; and on $x = 0$, $\phi_1 = 0 \leqslant \phi_2$. Hence it follows that the solution of (20) satisfies

$$\phi \geqslant \log\left(\frac{a + e^{(1+a)t}}{1 + a}\right) \operatorname{erf}\left(\frac{x}{2t^{\frac{1}{2}}}\right).$$

3. A much better result, in the sense that it is a closer lower bound can be constructed by finding a function which takes the same values on the boundary as that taken by the function to be found. For this, take

$$\phi_1 = t + \operatorname{erf}\left(\frac{x}{2t^{\frac{1}{2}}}\right) \left(\log\left(\frac{a + e^{(1+a)t}}{1 + a}\right) - t\right).$$

That is, $\phi_1 = t$ on $x = 0$,

$\phi_1 = 0$ on $t = 0$.

As in the previous case, it can be shown that $F(\phi_1) \geqslant 0$, and hence

$$t + \operatorname{erf}\left(\frac{x}{2t^{\frac{1}{2}}}\right) \left(\log\left(\frac{a + e^{(1+a)t}}{1 + a}\right) - t\right) \leqslant \phi.$$

Then $\exp\left[\operatorname{erf}\left(\frac{x}{2t^{\frac{1}{2}}}\right)\left(t - \log\left(\frac{a + e^{(1+a)t}}{1 + a}\right)\right) - t\right] \geqslant \lambda.$

To obtain bounds for θ take an equation in the form given by (13). For if

$$M(\theta) \equiv \frac{\partial^2\theta}{\partial x^2} - \frac{\partial\theta}{\partial t} + a\lambda\theta = 0, \qquad \text{. . . . (3.24)}$$

and an upper bound is taken for λ, say λ', then a function satisfying

$$M'(\theta) \equiv \frac{\partial^2\theta}{\partial x^2} - \frac{\partial\theta}{\partial t} + a\lambda'\theta \leqslant 0 \qquad \text{i.e. } \theta',$$

will be a bound for the solution of equation (24). This is shown as follows:

$$M(\theta) = M'(\theta) + a(\lambda - \lambda')\theta \qquad \text{for any } \theta,$$

and so

$$M(\theta') = M'(\theta') + a(\lambda - \lambda')\theta'.$$

Noting that $\lambda - \lambda' \leqslant 0$ it follows that if a trial function θ' can be found satisfying $M'(\theta') \leqslant 0$, then $M(\theta') \leqslant M(\theta)$. Providing $\theta' \geqslant \theta$ on the boundaries the same inequality, $\theta' \geqslant \theta$, will hold everywhere. Likewise by taking a lower bound for λ; if it is possible to find a function θ' satisfying $M'(\theta') \geqslant 0$, it follows that θ' is a lower bound for the solution θ.

By appropriate choices of λ', bounds are found for θ below:

1. Consider $\lambda' = e^{-t}$. This is clearly an upper bound for λ as it is in fact the value of λ on the boundary $x = 0$.

$$M'(\theta) = \frac{\partial^2\theta}{\partial x^2} + ae^{-t}\theta - \frac{\partial\theta}{\partial t}.$$

Now the solution of $M'(\theta) = 0$ will be an upper bound for the solution of $M(\theta) = 0$. However, it is not possible to obtain a simple analytical solution for this and so a function θ' is sought such that $M'(\theta') \leqslant 0$. Note that the solution of $M'(\theta) = 0$ as $x \to \infty$, tends to $u(t)$, where

$$u(t) = \exp a(1 - e^{-t}) \quad \text{and} \quad u(0) = 1. \qquad \ldots . (3.25)$$

Further u is actually an upper bound as required, but is very weak, for, as $t \to \infty$, u tends to e^a whereas θ (given by (24)) tends to 1 + a. This suggests that a closer bound could possibly be obtained by setting $\theta' = 1 + uv$, where v satisfies

$$\frac{\partial^2 v}{\partial x^2} + ae^{-t} = \frac{\partial v}{\partial t}, \quad v = 0 \quad \text{on } x = 0 \quad \text{and when } t = 0. \quad . \; . \; (3.26)$$

That is

$$v = a\,\mathrm{erf}\left(\frac{x}{2t^{\frac{1}{2}}}\right) + \frac{ae^{-t}}{2}\left(e^{-ix}\mathrm{erfc}\left(\frac{x}{2t^{\frac{1}{2}}} - it^{\frac{1}{2}}\right) + e^{ix}\mathrm{erfc}\left(\frac{x}{2t^{\frac{1}{2}}} + it^{\frac{1}{2}}\right) - 2\right). \quad . \; . \; . \; . \; (3.27)$$

Thus by using this θ' it follows that

$$M'(\theta') = u\left(\frac{\partial^2 v}{\partial x^2} - \frac{\partial v}{\partial t}\right) - v\frac{\partial u}{\partial t} + ae^{-t}(1+uv),$$

$$= -ae^{-t}u - ae^{-t}uv + ae^{-t}(1+uv), \text{ using (25) and (26)}$$

i.e. $M'(\theta') = ae^{-t}(1-u) \leqslant 0$ as $u \geqslant 1$.

However, $\theta' = \theta$ (=1) on x = 0 and t = 0 and so by Theorem 5; $\theta(x,t) \leqslant 1 + uv$ where u and v are given by (25) and (27) respectively. This bound will provide the best estimate for θ for small x only, for as $x \to \infty$, $1 + uv \to 1 + a(1 - e^{-t})\exp(a(1-e^{-t}))$. For t sufficiently large this last value is greater than θ_∞ given in (23), which also is an upper bound for θ. This is illustrated below.

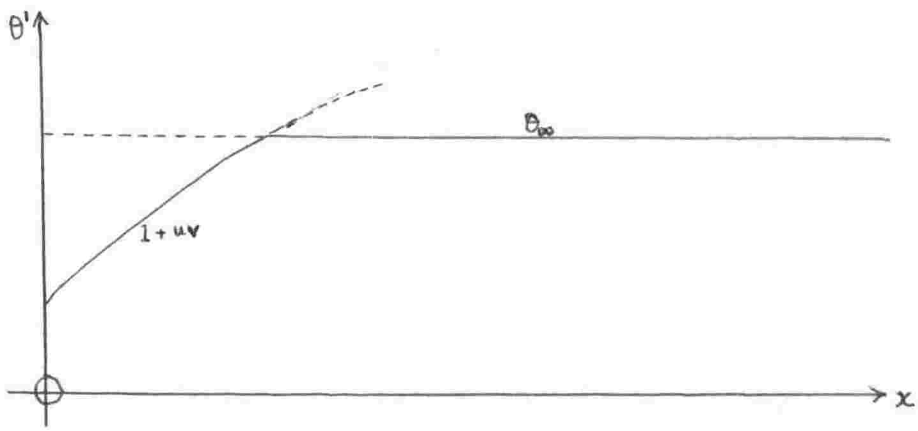


Fig. 3.8.

Hence to obtain the best upper bound at a point (x,t), select the smaller of $1+uv$ and θ_∞ at that point.

2. To obtain a lower bound for θ a lower bound is selected for λ. One such bound is λ_∞ given in (23). Then proceeding exactly as above it is possible to show that $\theta' = 1 + (y-1)z$ is a lower bound, where y satisfies

$$\frac{dy}{dt} = a\lambda_\infty y, \quad y(0) = 1 \quad \text{i.e. is } \theta_\infty; \qquad \ldots . \; (3.28)$$

and z satisfies

$$\frac{\partial^2 z}{\partial x^2} = \frac{\partial z}{\partial t}, \quad z = 0 \text{ on } x = 0 \text{ and } z = 1 \text{ when } t = 0. \qquad \ldots . \; (3.29)$$

Hence θ, the solution of (24) subject to $\theta = 1$ on $x = 0$ and when $t = 0$ satisfies

$$\theta \geqslant 1 + \frac{a(1 - e^{-(1+a)t})}{1 + ae^{-(1+a)t}} \operatorname{erf}\left(\frac{x}{2t^{\frac{1}{2}}}\right). \qquad \ldots . \; (3.30)$$

It is also of interest to consider the same problem in a finite domain, though still taken for convenience, in one dimension. Hence suppose that θ and λ satisfy the same equations, viz. (15) and (16) with $n = 1$, where $\theta = 1$ on $x = 0$ <u>and</u> $x = b$ as well as initially. Then consider examples exactly as in the semi-infinite problem.

1. By taking $\lambda' = e^{-t}$ (an upper bound) it follows that $\theta' = 1 + uv$ is an upper bound for θ, where $u = \exp(a(1 - e^{-t}))$ as before, and v is the solution of

$$\frac{\partial^2 v}{\partial x^2} + ae^{-t} = \frac{\partial v}{\partial t}, \quad v = 0 \text{ on } x = 0, b \text{ and when } t = 0.$$

Note the solution of this last problem is given by

$$v(x,t) = a\left(\frac{\cos(\frac{1}{2}b-x)}{\cos\frac{1}{2}b} - 1\right)e^{-t} - \frac{4b^2a}{\pi}\sum_{m=0}^{\infty}\frac{e^{-\frac{(2m+1)^2\pi^2 t}{b^2}}\sin(2m+1)\pi x/b}{(2m+1)\left[(2m+1)^2\pi^2 - b^2\right]}\ . \qquad \ldots\ (3.31)$$

Then $M'(\theta') = ae^{-t}(1-u) \leqslant 0$, as $u \geqslant 1$. However, $\theta' = \theta$ on $x = 0,b$ and when $t = 0$ and so it follows that $1+uv \geqslant \theta$ everywhere.

2. As in the semi-infinite problem, a lower bound is obtained for θ by taking as a lower bound for λ the expression λ_∞. Then it is possible to show that $\theta' = 1 + (y-1)z$ is a lower bound where y,z are given by (28) and (29), but now $z = 0$ on $x = 0$ <u>and</u> $x = b$. That is,

$$z = \frac{4}{\pi}\sum_{m=0}^{\infty}\frac{\sin(2m+1)\pi x/b}{2m+1}e^{-\frac{(2m+1)^2\pi^2}{b^2}t}.$$

For $M'(\theta') = a\,'(1-z) \geqslant 0$ as $z \leqslant 1$, and $\theta = \theta'$ on the boundaries $x = 0,b$ and when $t = 0$. Hence $\theta \geqslant 1 + (y-1)z$ everywhere.

Thus it can be seen that, although no direct comparison theorem is possible, upper and lower bounds can be obtained for the temperature and reactant concentration.

Chapter 4

BOUNDARY CONDITIONS AND THE BOUNDARY LAYER

At this stage it is necessary to investigate the physical implications when the temperature is prescribed on the boundary. In reality, it is not always possible to ignore the thermal propeties of the surrounding medium. In a recent paper Philip[16] examined the heat conduction between a sphere and a surrounding medium of different thermal properties. The sphere was assumed to be at a higher temperature initially. Philip found the temperature and heat flux on the surface of the sphere as a function of time.

Suppose that the inner sphere is of thermal conductivity and diffusitivity given by k and $\mathcal{K}$ respectively. Likewise the corresponding quantities for the surrounding medium (supposed to be infinite in extent) are k_1 and $\mathcal{K}_1$. Then the boundary conditions on the surface of the sphere (r=a) are that

(i) $\left[\theta\right]_{r=a-0} = \left[\theta\right]_{r=a+0}$ i.e. the temperature is continuous,

(ii) $k\left[\frac{\partial\theta}{\partial r}\right]_{r=a-0} = k_1\left[\frac{\partial\theta}{\partial r}\right]_{r=a+0}$ i.e. the flux is continuous.

The first of these expresses the fact that there is no sudden jump in the temperature on the surface, while the second states that there is no accumulation of energy at the surface. In order to ascertain what physical assumption is made when the surrounding medium is neglected, two separate problems will be considered: one is based on a model similar to that of Philip's, and the other on a model, typical of those usually considered.

4.1. Different Boundary Conditions

A comparison will be made for the two problems described below, by calculating the temperature and flux in the semi-infinite region $x > 0$, with a point source placed at $x = x_o (>0)$ and switched on instantaneously at $t = 0$. The temperature and flux due to this source will be found and the expressions can be compared directly.

(a) $x > 0$, thermal conductivity k, thermal diffusivity κ.

$x < 0$, " " k_1, " " κ_1.

The equation governing the diffusion of heat in the region can be written

$$\frac{\partial^2 G_1}{\partial x^2} - \frac{1}{\kappa}\frac{\partial G_1}{\partial t} = - \delta(x-x_o)\delta(t), \qquad \ldots . (4.1)$$

with the boundary conditions: G_1 and $k\partial G_1/\partial x$ are continuous on $x = 0$. In (1) k and κ are interpreted as k_1 and κ_1 for $x < 0$, and the right hand side is merely the two-dimensional delta function. Hence $G_1(x,t;x_o,0)$ will be the Green's function for this problem. It corresponds to the temperature distribution in a region, initially at zero temperature, when at $t = 0$ a concentrated heat source is applied suddenly and instantaneously at the point $x = x_o$.

(b) Consider just the region $x > 0$, of thermal constants k and κ. Again the equation can be written as in (1) with G_2 for G_1, but now the boundary condition is written $k\partial G_2/\partial x = HG_2$ on $x = 0$ (see note 3 on page 6). H is called the surface cooling coefficient. G_2 is the Green's function for this problem, different from that of (a) because of the different boundary conditions.

These problems can be solved by taking Laplace transforms of equation (1) and solving the resulting ordinary differential equation in x, using the appropriate boundary conditions. On inverting the transforms so obtained it is found that the solutions are given by:

$$\text{(a)} \quad G_1 = \tfrac{1}{2}\left(\frac{\kappa}{\pi t}\right)^{\frac{1}{2}}\left(e^{-\frac{(x-x_0)^2}{4\kappa t}} + \frac{\sqrt{\frac{\kappa_1}{\kappa}} - \frac{k_1}{k}}{\sqrt{\frac{\kappa_1}{\kappa}} + \frac{k_1}{k}} e^{-\frac{(x+x_0)^2}{4\kappa t}}\right), \text{ for } x > 0. \quad . . (4.2)$$

$$\text{(b)} \quad G_2 = \tfrac{1}{2}\left(\frac{\kappa}{\pi t}\right)^{\frac{1}{2}}\left(e^{-\frac{(x-x_0)^2}{4\kappa t}} + e^{-\frac{(x+x_0)^2}{4\kappa t}}\right) + \frac{H\kappa}{k} e^{(x+x_0)\frac{H}{k} + \frac{H^2\kappa t}{k^2}} \operatorname{erfc}\left(\frac{x+x_0}{2\sqrt{\kappa t}} + \frac{H}{k}\sqrt{\kappa t}\right). \quad . . . . (4.3)$$

Now these two expressions can be seen to be equal if we put $k_1 = 0$ in (a) and $H = 0$ in (b). For both are now equal to $\tfrac{1}{2}\left(\frac{\kappa}{\pi t}\right)^{\frac{1}{2}}\left(e^{-\frac{(x-x_0)^2}{4\kappa t}} + e^{-\frac{(x+x_0)^2}{4\kappa t}}\right)$. This was expected, of course, because these two conditions mean that the boundary condition at $x = 0$, for both problems is $\partial G/\partial x = 0$. That is, the surface $x = 0$ is thermally insulated from; (a) the second medium in the first case, and (b) from its surroundings in the second case. Also, if in (b), H tends to infinity, the expression G_2 tends to the expression $\tfrac{1}{2}\left(\frac{\kappa}{\pi t}\right)^{\frac{1}{2}}\left(e^{-\frac{(x-x_0)^2}{4\kappa t}} - e^{-\frac{(x+x_0)^2}{4\kappa t}}\right)$; that is, the same as G_1 when κ_1 is set equal to zero. H tends to infinity corresponds to the case in which G_2 is prescribed on the boundary $x = 0$ (in this case $G_2 = 0$ on $x = 0$). Exactly the same happens when the flux $k\partial G/\partial x$ is considered in the two cases. Hence, it follows that if the temperature is prescribed on the boundary, that this is equivalent to neglecting the thermal diffusivity of the neighbouring medium.

This can be argued from physical considerations also. For if κ_1 is negligible (compared to k_1), this corresponds to a medium with a large thermal capacity C. Hence any heat which is transferred across the boundary $x = 0$ will not produce any significant change in the temperature in the region $x < 0$.

4.2. The Boundary Layer

In the preceding section, consideration was given to the physical reality of the boundary conditions imposed on the surface of the medium. In any problem, for which it is desired to find the temperature at any point as a function of time, one of the first things of interest is the effect of the boundary and the conditions imposed there. In particular, how long does it take for these conditions to have an appreciable effect on the solution at any given point? The equation for the temperature being parabolic, implies that the effects due to the boundary are felt immediately throughout the medium. However, in practice, one looks for the points for which the boundary conditions have had a significant effect on the solution there. Such points are said to be within the boundary layer. Outside the boundary layer, the solution behaves as though the boundary is not there at all.

For example, take the problem of a semi-infinite region with a constant heat source and homogeneous boundary and initial conditions, i.e.

$$\frac{\partial^2\theta}{\partial x^2} + 1 = \frac{\partial\theta}{\partial t} \qquad \ldots . (4.4)$$

subject to $\theta = 0$ on $x = 0$ and at $t = 0$. The solution is found by taking a Laplace transform in t so that

$$\frac{d^2\bar{\theta}}{dx^2} - p\bar{\theta} = -\frac{1}{p}, \qquad \ldots . (4.5)$$

where $\bar{\theta}(x,p) = \int_0^\infty \theta(x,t)e^{-pt}dt.$ . . . . (4.6)

On solving (5) it follows that $\bar{\theta} = \frac{1}{p^2}(1 - e^{-\sqrt{p}\,x})$ and so by inverting this transform, using Erdelyi's tables[17],

$$\theta(x,t) = t + x\left(\frac{t}{\pi}\right)^{\frac{1}{2}} e^{-x^2/4t} - (t+\tfrac{1}{2}x^2)\operatorname{erfc}(x/2t^{\frac{1}{2}}). \quad . . . . (4.7)$$

The expression in (7) is, of course, the complete solution. However much is to be gained from looking at the solution more closely. The solution independent of x is $\theta = t$, obtained from (7) as the asymptotic value as x tends to infinity. At any given time, it is possible to obtain a measure of the behaviour of the solution as x becomes large. This is done by considering the asymptotic expression for erfc(z) for z large. Hence, from (7),

$$\theta(x,t) = t\left(1 - \frac{1}{8\pi^{\frac{1}{2}}z^3}\, e^{-z^2} \ldots\right), \quad . . . . (4.8)$$

where $z = x/2t^{\frac{1}{2}}$ and terms of $O\left(\frac{e^{-z^2}}{z^5}\right)$ have been neglected. Then by choosing a "level of significance" s, that is, for $z \geqslant y$, where $e^{-y^2}/8\pi^{\frac{1}{2}}y^3 = s$, the second term in (8) can be neglected, a measure of the width of the boundary layer is obtained. In the x,t plane, the boundary layer will be marked by the parabola $x^2 = 4y^2t$. This is illustrated in Fig. 4.1. The corresponding solution as a function of position, at any fixed time is illustrated in Fig. 4.2.

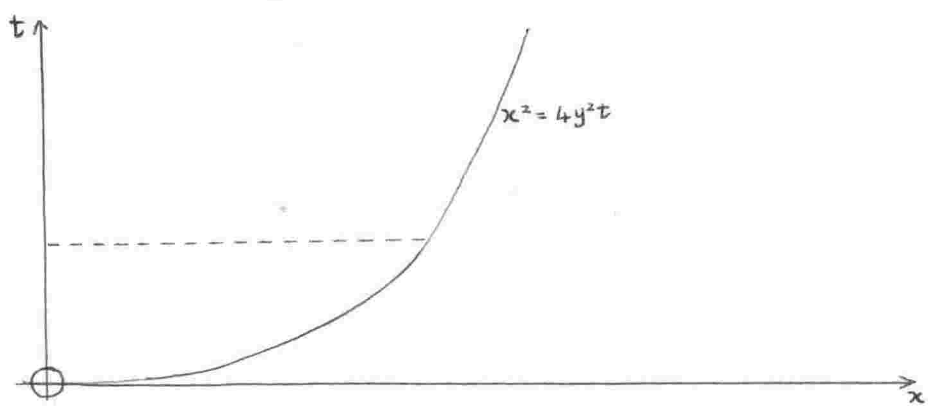


Fig. 4.1.

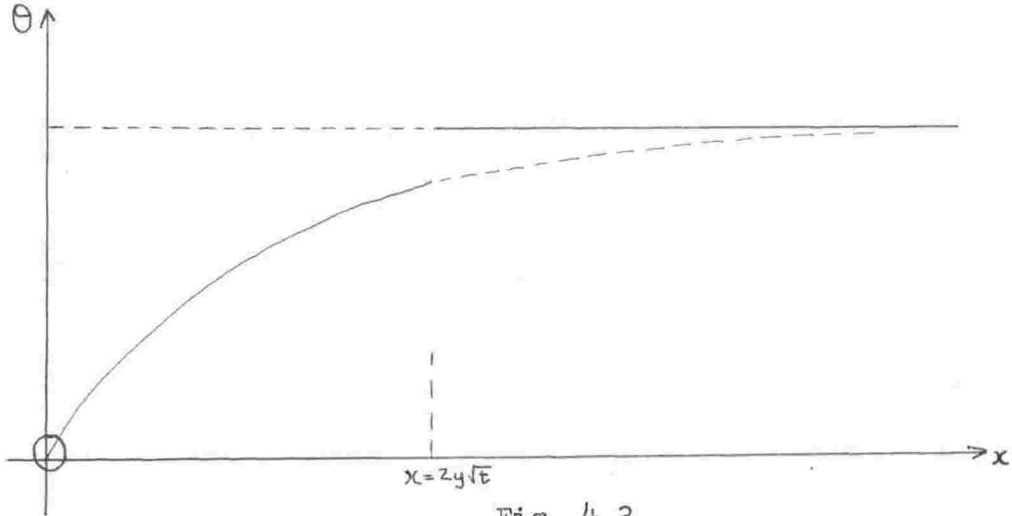


Fig. 4.2.

The boundary layer is like a wave advancing into the medium with speed inversely proportional to $(t)^{\frac{1}{2}}$.

The solution in (8) is, of course, only valid for z large and so is not applicable near the boundary x = 0. Outside the boundary layer the solution can be approximated by the solution independent of x, i.e. $\theta = t$.

To obtain an equivalent form of the solution (7) near the boundary x = 0, use is made of the asymptotic expansion for erfc(z) when z is small. Hence,

$$\theta \quad = \quad t(\; 2z/\pi^{\frac{1}{2}} - z^2/2 + z^3/12\pi^{\frac{1}{2}} \; \ldots \;). \qquad \ldots . \; (4.9)$$

The above is valid only for z small and so is not applicable near t = 0. It is therefore of use within the boundary layer only.

From this simple example an indication is given on a technique useful in any problem of the type discussed here. For it is usually possible to find the asymptotic value of the solution as x tends to infinity. Equation (1.4) implies that the solution of the system described by (1.1) and (1.7) independent of x is given by

$$\frac{\partial\theta}{\partial t} = -\alpha\frac{\partial\lambda}{\partial t} , \qquad \ldots . (4.10)$$

where in the diffusion equation t is written for $\mathcal{K}t$ as before. This means $\theta + \alpha\lambda$ is constant for all t and so is equal to its initial value. Thus by substituting for θ in the equation given in (1.1),

$$\frac{\partial\lambda}{\partial t} = -g(\theta,\lambda) , \qquad \ldots . (4.11)$$

it is possible to find both θ and λ. In equation (11) $g(\theta,\lambda)$ is written for the limit as x tends to infinity of the expression $g(x,\theta,\lambda)$ introduced in Chapter 1.

These ideas can be of use in other geometries in a similar manner. For example, in a finite slab which is of sufficient thickness so that the boundary layers associated with each boundary do not overlap for small time. Suppose the slab is of thickness b, then the boundary layers spread into the region as shown in Fig. 4.3.

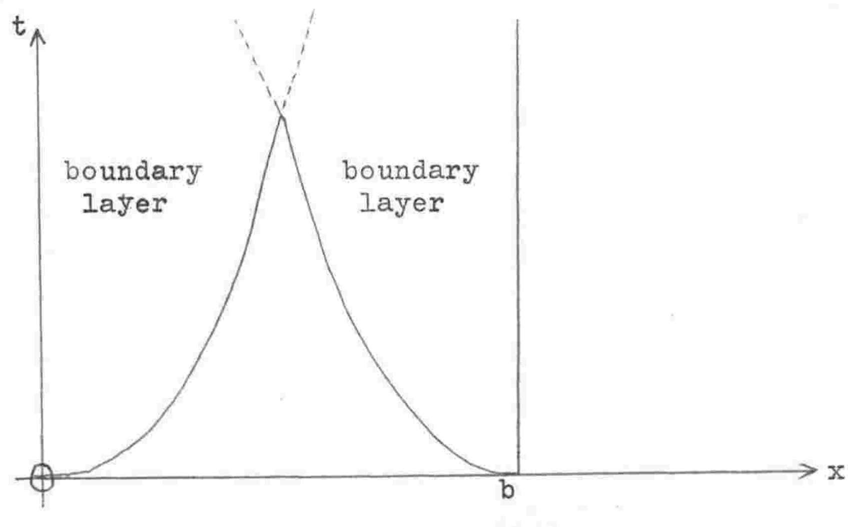


Fig. 4.3.

Hence it is only in the triangular-shaped region (small time) that one can use the solution independent of time.

4.3. The Thin Slab and the Techniques of Perturbation.

The other remaining case to be considered is when the slab is thin. This means that the effect of the boundary is felt almost immediately throughout the whole slab. A perturbation expansion can be used to obtain an approximate solution to the problem. This has to be done in such a way so as to avoid obtaining a singular perturbation series.

Consider the example from Chapter 3, that is the coupled pair of equations

$$\frac{\partial^2\theta}{\partial x^2} = \frac{\partial\theta}{\partial t} + a\frac{\partial\lambda}{\partial t}\,, \qquad \ldots . \ (4.12)$$

$$\frac{\partial\lambda}{\partial t} = -\lambda\theta\,, \qquad \ldots . \ (4.13)$$

in the region $0 < x < b$ subject to $\theta = 1$ on $x = 0$ and $x = b$, and $\theta = 1$, $\lambda = 1$ when $t = 0$. Recognition of the fact that the specimen is small is given in writing $\theta = 1 + \varepsilon u$ and $\varepsilon^{\frac{1}{2}}x$ for x, where ε is small and u is a function of x,t satisfying:

$$\frac{\partial^2 u}{\partial x^2} = \varepsilon\frac{\partial u}{\partial t} + a\frac{\partial\lambda}{\partial t}\,, \qquad \ldots . \ (4.14)$$

$$\frac{\partial\lambda}{\partial t} = -\lambda(1 + \varepsilon u)\,, \qquad \ldots . \ (4.15)$$

with homogeneous boundary and initial conditions. Now in (14), if the expansions

$$u = u_o + \varepsilon u_1 + \varepsilon^2 u_2 + \ldots, \qquad \ldots . \ (4.16)$$

$$= \lambda_o + \varepsilon\lambda_1 + \varepsilon^2\lambda_2 + \ldots, \qquad \ldots . \ (4.17)$$

are substituted and the coefficients of corresponding powers of are equated, it follows that,

$\dfrac{\partial^2 u_o}{\partial x^2} = a\dfrac{\partial \lambda_o}{\partial t}$, $\dfrac{\partial^2 u_i}{\partial x^2} = \dfrac{\partial u_{i-1}}{\partial t} + a\dfrac{\partial \lambda_i}{\partial t}$ for $i = 1,2, \ldots$. This gives rise to what is called a singular perturbation series. A discussion of these is given in Van Dyke[18]. To avoid this, β is written for $\mathcal{E}$ in equation (14) only, and is considered as a constant. Then on equating corresponding powers of ε as before it follows:

$$\frac{\partial^2 u_o}{\partial x^2} = \beta\frac{\partial u_o}{\partial t} + a\frac{\partial \lambda_o}{\partial t}, \quad \ldots . (4.18)$$

$$\frac{\partial \lambda_o}{\partial t} = -\lambda_o, \quad \ldots . (4.19)$$

$$\frac{\partial^2 u_i}{\partial x^2} = \beta\frac{\partial u_i}{\partial t} + a\frac{\partial \lambda_i}{\partial t}, \quad \ldots . (4.20)$$

$$\frac{\partial \lambda_i}{\partial t} = -(\lambda_i + u_{i-1}\lambda_o + \ldots\ldots + u_o\lambda_{i-1}) . \quad \ldots . (4.21)$$

Equations (20) and (21) apply for $i = 1,2, \ldots$. u_i has homogeneous boundary and initial conditions (i=0 included) and $\lambda_o = 1$, $\lambda_i = 0$ when $t = 0$.

On solving (19) subject to the above initial condition it is found that $\lambda_o = e^{-t}$. Then substituting in (18), taking Laplace transforms it follows that

$$\frac{d^2\bar{u}_o}{dx^2} + \frac{a}{p+1} = \beta p\bar{u}_o, \quad \text{subject to } \bar{u}_o = 0 \text{ on } x = 0 \text{ and } x = b;$$

where $\bar{u}_o = \int_0^\infty e^{-pt}u_o(x,t)dt$. So

$$u_o(x,t) = \frac{a}{\beta}\left(\frac{\cos(\frac{1}{2}b-x)\beta^{\frac{1}{2}}}{\cos\frac{1}{2}b\beta^{\frac{1}{2}}} - 1\right)e^{-t} - \quad \ldots . (4.22)$$

$$\frac{4b^2a}{\pi}\sum_{n=0}^{\infty}\frac{e^{-(2n+1)^2\pi^2t/\beta b^2}\sin(2n+1)\pi x/b}{(2n+1)\left[(2n+1)^2\pi^2 - \beta a^2\right]} .$$

This expression, in (22), represents an approximation to the solution of the problem as posed previously. It is the <u>first-order</u> approximation to the solution. Mathematically, it is the solution of the diffusion equation subject to heat generation which depends on the surface temperature and the surface reactant concentration. How good this approximation is, depends on the thickness of the specimen.

A better approximation can be obtained by solving for the second-order terms λ_1, u_1; given by the coupled equations (20) and (21) with $i = 1$. This is done by taking Laplace transforms of the equations and solving, exactly as before. In (21), use is made of the solution u_o given in (22), or rather the Laplace transform of u_o, to form a first order linear ordinary differential equation for λ_1. As one proceeds for higher order approximations, the problems of computation increase, and so it is not intended to state the higher terms, except to note that it is possible to solve for these in principle. Further, if the u_o, u_1, ... so obtained when $\beta \neq 0$ are expanded in powers of β, the term independent of β should be that obtained by putting $\beta = 0$ in (18 - 21). For example, $u_o|_{\beta=o} = \frac{1}{2}ax(b-x)e^{-t}$ and this is the solution of $\dfrac{\partial^2 u_o}{\partial x^2} = a\dfrac{\partial \lambda_o}{\partial t} = -a\lambda_o$, subject to homogeneous boundary conditions on $x = 0$ and $x = b$.

To use these perturbation series as approximations to the solution, it is necessary to put $\beta = \varepsilon = 1$. It is interesting to note that $u_o|_{\beta=1}$ is the same expression as that denoted by v in Chapter 3 (see pp. 41 - 42).

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Thus the finite slab can be "solved" in the following ways:

(i) if it is thin, then the perturbation series obtained in this section can be used;

(ii) if it is thick, then near the edges the boundary layer solution is a useful approximation,and in the centre the solution approximates an infinite problem for sufficiently small time. For large time the specimen will behave like a thin specimen, in that the effect of the boundary is felt throughout; though it may be that owing to the equation being nonlinear, the perturbation series will not be valid there.

These ideas can be generalized to any type of reaction in any particular geometry, provided that it is possible to obtain linear equations for the terms in the perturbation series.

Chapter 5.

THE SPACE - AVERAGING PROCESS AND CRITICAL STATES

As it was mentioned in Chapter 1, many of the authors who have studied this particular system have made use of what will be called a space - averaging process. It is intended to explain this in detail and comment on its validity. These authors have been interested mainly in determining the critical conditions. So before any discussion of the space - averaging process can be given, a definition of what is meant by critical conditions must be made.

5.1. The Critical State.

There is some difficulty in defining the critical state, and just this problem has occupied the attention of many authors in the last few years. A state will be said to subcritical if the corresponding solution is stable, and supercritical if the corresponding solution is unstable. The extreme case of stability shall be called critical stability. However, the question is left as to how to decide whether or not a given solution is stable or unstable. This shall be defined here as in Bellman[19]. That is, a solution, θ, of a partial differential equation is said to be stable, if any solution, Θ, of the equation whose boundary values are sufficiently "close" to θ's boundary values, remains "close" to θ for all values of the independent variables. The term "close" will be used in the following sense: θ_1 and θ_2 are sufficiently close in a set B if the maximum of $|\theta_1 - \theta_2|$ is sufficiently small. It should be noted that stability is not necessarily the same as being bounded.

Stoker[20] set up a criterion for the stability of an equilibrium state of a mechanical system through the application of the method of small oscillations. This has been extended to cover situations governed by systems of partial differential equations. In McNabb[21], the criterion is justified for a class of parabolic equations. Consider the equation for a zero order reaction, which from Chapter 1 can be written

$$\Delta\theta + f(x,\theta) = \frac{\partial\theta}{\partial t}. \qquad \ldots . \; (5.1)$$

Then the stability of the steady state solutions of (1) can be decided from considerations concerning the solutions of the equation

$$\Delta\theta + f(x,\theta) = 0. \qquad \ldots . \; (5.2)$$

In particular, each member of a one parameter family of steady state solutions is stable in any closed region not containing points at which the member touches the envelope of the family. As an example, McNabb discussed the equation

$$\frac{\partial^2\theta}{\partial x^2} + \delta e^{\theta} = \frac{\partial\theta}{\partial t}, \qquad \ldots . \; (5.3)$$

in a slab of thickness 2b. This is the equation derived from the Arrhenius equation (1.2), by making a binomial approximation. The steady state solution of (3) was given in Kamenetskii[1] as

$$\theta = \theta_0 - 2\log\cosh\left[(\delta e^{\theta_0}/2)^{\frac{1}{2}}x\right], \qquad \ldots . \; (5.4)$$

where θ_0 satisfies $e^{\theta_0} = \cosh^2(\delta e^{\theta_0}/2)^{\frac{1}{2}}b$. Then δ_{crit} is the maximum δ for which a solution of this last equation is real i.e. require $y = \cosh^2(\delta b^2 y/2)^{\frac{1}{2}}$ to have a real solution. By defining $\sigma = (\delta b^2 y/2)^{\frac{1}{2}}$, it follows that $\cosh\sigma/\sigma = (2/\delta b^2)^{\frac{1}{2}}$. Hence to find the maximum δ, all that is necessary is to find the minimum of $\cosh\sigma/\sigma$ for all positive σ. This is found by successive iterations to be 1·51, and hence $\delta_{crit} = 0{\cdot}88/b^2$. Or if the value of δ is fixed, it follows that the critical size of the slab is given by $b = 0{\cdot}94/\delta^{\frac{1}{2}}$. That is if $\delta b^2 > 0{\cdot}88$ the solutions of (3) are unstable and in fact, as is shown in McNabb, are unbounded as t tends to infinity. If $\delta b^2 \leq 0{\cdot}88$ the solution is stable and tends to the steady state given in (4), as t tends to infinity. The critical state is given, of course, by $\delta b^2 = 0{\cdot}88$. This is illustrated in the figure below.

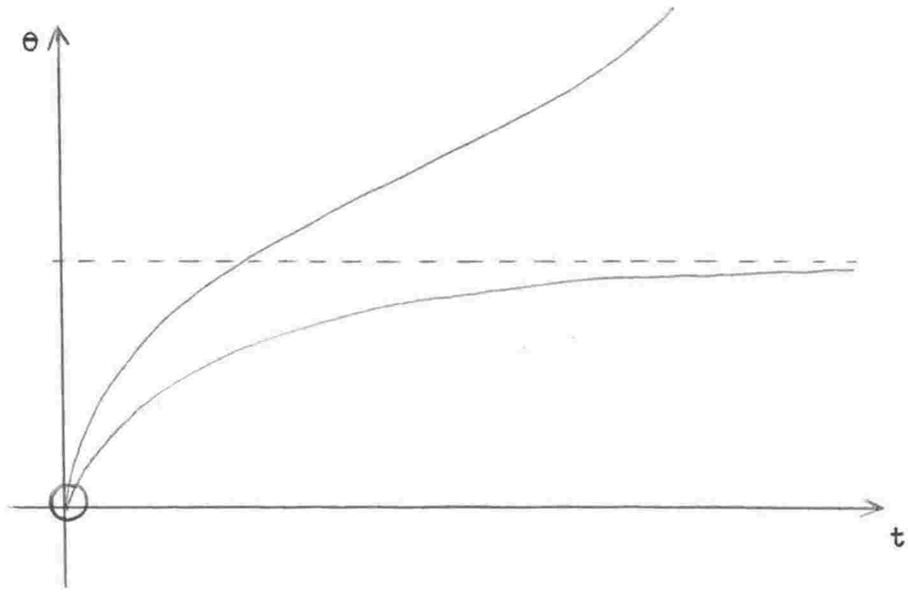


Fig.5.1.

In this case it is obvious that if the system is stable, it means that the solution is in fact bounded, and if it is unstable, that the solution is unbounded, though this is not generally the case.

Thus there is no problem in classifying any zero order reaction, but in the general case of a nth order reaction the picture is far from clear. The following comments will apply to the most general type of system, that is as described in Chapter 1. When the corresponding temperature-time curves are drawn, it is obvious that the behaviour is different from that illustrated in Fig.5.1. The temperature first rises as though it was a zero order reaction, then owing to the reactant consumption becoming significant, this effect gradually dominates. Thus the temperature reaches a maximum and then tends asymptotically to zero. This is shown in Fig. 5.2.

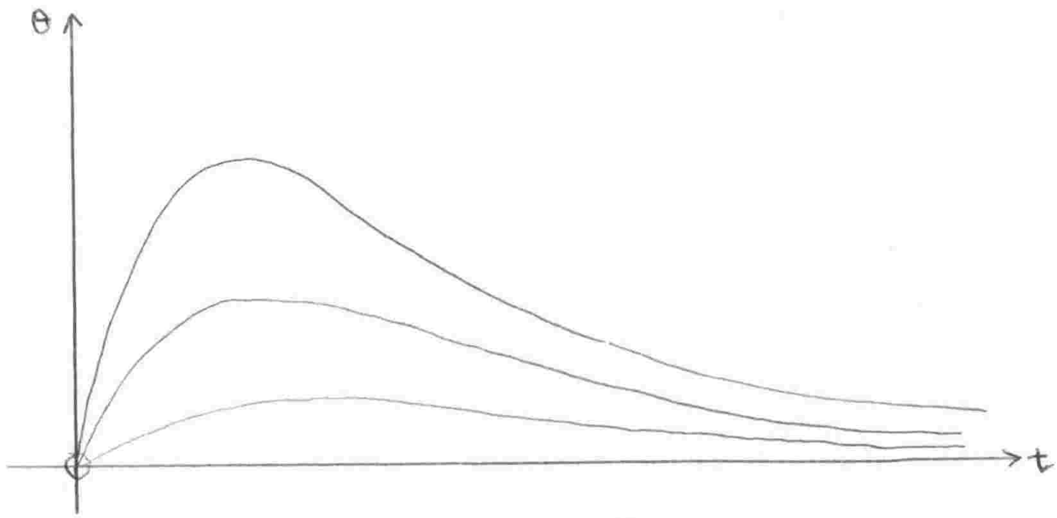


Fig. 5.2

Thus any disturbance added to any particular state will eventually shrink to zero as t increases, and it is never possible for any such disturbance to grow exponentially with t. Using the definition of stability given on p.54, one must conclude that any reaction of nonzero order is necessarily stable. However in the paper by Thomas and Bowes[8] an attempt is made to set up a criterion for critical stability. It is intended to discuss this further.

For conditions, which are defined by Thomas and Bowes to be stable, curves of θ_o (the centre temperature) against t increase to a maximum (and then fall) in such a way that $\partial\theta_o/\partial t$ decreases as t increases, i.e. $\partial^2\theta_o/\partial t^2 < 0$. However, if the conditions are unstable (again in the sense of Thomas and Bowes) θ_o plotted against t passes through a point of inflection and then rises much more rapidly to a maximum which is much higher than in the stable case.

This type of temperature behaviour is conventionally considered as characteristic of ignition, and the lowest value of any parameter (such as δ before) for which a curve of θ_o against t includes such an inflection while the temperature is rising is then defined, again conventionally, as the critical state. With the type of reaction that is considered here, this is a reasonable approximation. For the rate at which heat is evolved is <u>nondecreasing</u> with temperature. However, if there was a more marked variation of heat production with temperature, then the criterion would become ambiguous.

This criterion can be thought of in a different way, although the same conclusions, as to which states are stable and which are unstable, are reached. For the stable case, any small disturbance added to the system will tend to decrease with time. One could say that the disturbed state grows back on to the undisturbed state. In the unstable case, any such disturbance will first grow away from the undisturbed state and then gradually decrease to zero for large time. Such behaviour can be called "variation increasing" as compared to "variation decreasing" in the former case. Thomas et.al. wish to distinguish between these two cases. It is suggested here that what they are really saying is that the system shall be stable or unstable according to whether it is asymptotically stable or unstable. The word "asymptotically" is used here in the sense that a zero order reaction can be regarded as the limit of a sequence of nth order reactions. This will be discussed below where a particular example will be discussed which illustrates asymptotic instability.

Consider the coupled system,

$$\frac{\partial^2\theta}{\partial x^2} + \lambda^n\theta = \frac{\partial\theta}{\partial t}, \qquad \ldots . (5.5)$$

$$\frac{\partial\lambda}{\partial t} = -\alpha\lambda^n\theta \qquad \ldots . (5.6)$$

where α is a parameter; in a finite slab of thickness 2b, with $\theta = 1$, $\lambda = 1$ when $t = 0$ and $\theta = 1$ on $x = b$. Now, in general, under the criterion of Bellman, this system is said to be stable for any $\alpha \neq 0$. If $\alpha = 0$, then the reaction is effectively of zero order, and so the problem is similar to that proposed at the beginning of this section. For this case,

$$\frac{\partial^2\theta}{\partial x^2} + \theta = \frac{\partial\theta}{\partial t}, \qquad \ldots . (5.7)$$

subject to $\theta = 1$ on $x = b$ and $\theta = 1$ when $t = 0$. Then as in McNabb, the stability of the steady state solutions of (7) can be decided from

$$\frac{d^2\theta}{dx^2} + \theta = 0. \qquad \ldots . (5.8)$$

A family of solutions satisfying the boundary condition $\partial\theta/\partial x = 0$ at $x = 0$ and symmetrical about $x = 0$ is $\theta(x,A) = A\cos x$. The steady state solution $\theta(x,A)$ touches the envelope at $x = \pm\pi/2$, $\theta = 0$ (in fact the envelope is just these two points in this case) and is therefore stable in any region $|x| \leq b$ if $b < \pi/2$. The corresponding solution satisfying $\theta = 1$ on $x = b$ is $\theta = \cos x/\cos b$. Thus it is said that the critical size of the region is $b = \pi/2$. For this value of b, the solution of (7) is unbounded as t tends to infinity.

Now, returning to the case $\alpha \neq 0$ and taking a region which exceeds the critical size, i.e. is unstable, when $\alpha = 0$, then it may be said that the system is asymptotically unstable as α tends to zero. Then the curves for various α will be shown in Fig. 5.3.

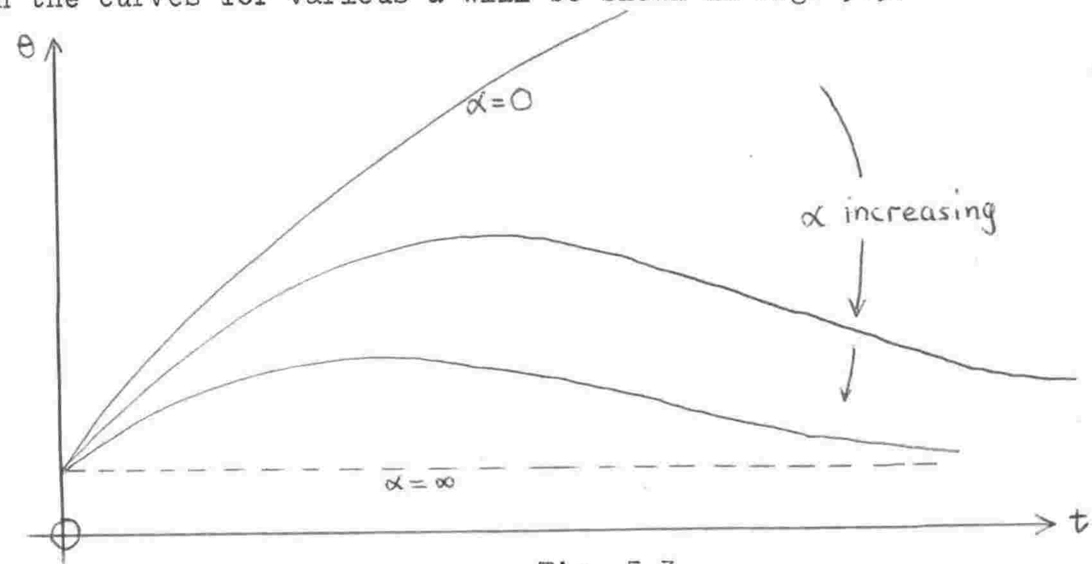


Fig. 5.3

Thus it can be seen how the criterion set up by Thomas hinges on the corresponding zero order reaction. Suppose that the time scale of reactant consumption is large compared to that of the time taken to reach a quasi-steady state (that is the temperature curve flattens off). Note that this corresponds to α small in the above example. Then for small time the temperature behaves as though the reaction was of zero order, in that if a small disturbance is added, this tends to grow exponentially, or disappears, with time depending whether or not the reaction is stable.

5.2. The Space-averaging Process

The authors with which this thesis will be mainly concerned are Thomas and Bowes[3,8,9] and Adler and Enig[4]. The primary aim of these authors is to convert the partial differential equations into ordinary differential equations in the independent variable t, thereby making the equations easier to solve. This is done by an integration over space and replacing the temperature and reactant concentration by the averages of these quantities over the whole region. Consider the equations for a heated body, which can be written, using suitable dimensionless variables as

$$\Delta\theta = \frac{\partial\theta}{\partial t} + a\frac{\partial\lambda}{\partial t}, \qquad \ldots . (5.9)$$

$$\frac{\partial\lambda}{\partial t} = -\lambda^n f(\theta). \qquad \ldots . (5.10)$$

In (9) the Laplacian is in the appropriate dimension. For a symmetrically heated body, $\Delta\theta \equiv \partial^2\theta/\partial x^2 + \frac{j}{x}\,\partial\theta/\partial x$ where $j = 0,1,2$ for a slab, cylinder, and sphere respectively. The region occupied by the material will be denoted by V and its boundary by S. The function $f(\theta)$ is in general a nonlinear function of temperature e.g. as the Arrhenius equation $f = Ae^{-B/\theta}$. These equations are to be solved subject to a prescribed value of θ on S and prescribed values of θ and λ initially.

Now this is done in the authors mentioned previously, but it is felt that at no stage is it clear just what assumptions are made, and how the system arrived at resembles that with which they started. So by integrating throughout the whole region V and using Gauss' theorem in the appropriate dimensions it follows that

$$\frac{1}{V}\int_S \operatorname{grad}\theta . d\underset{\sim}{S} = \frac{d\tilde{\theta}}{dt} + a\frac{d\tilde{\lambda}}{dt}. \qquad \ldots . (5.11)$$

In (11) V is used for the volume of the region and $\tilde{\theta}, \tilde{\lambda}$ are the average temperature and reactant concentration. Likewise, by using (10) it follows that

$$\frac{d\tilde{\lambda}}{dt} = -\frac{a}{V}\int_V \lambda^n f(\theta)\,dV. \qquad \ldots . (5.12)$$

The introduction of the quantities $\tilde{\theta}$ and $\tilde{\lambda}$ explains the use of the term "space-averaging process". At this point two assumptions are made. These are outlined below.

(i) The second term in equation (12) can be written $-aA\tilde{\lambda}^n f(\tilde{\theta})$, where $A(t) \equiv \int_V \lambda^n f(\theta)dV/V\tilde{\lambda}^n f(\tilde{\theta})$. If the region is large enough, then for sufficiently small time before the boundary has had a significant effect on θ and λ, $A(t) \approx 1$. Indeed this is the first approximation made. However, it can be noted that this is equivalent to using a perturbation expansion in which the first term represents the solution independent of x, while the higher order terms represent the effect of the boundary layer as it moves into the region. For if $x/\varepsilon^{1/2}$ is written for x in (9) and (10), and corresponding power series expansions are written for θ and λ it follows that

$$A(t) \quad = \quad 1 + \varepsilon A_1(t) + \varepsilon^2 A_2(t) + \ldots \qquad \ldots . (5.13)$$

Hence, the approximation made is to neglect all terms but the first in (13), and so,

$$\frac{d\tilde{\lambda}}{dt} \quad = \quad - a\,\tilde{\lambda}^n f(\tilde{\theta}) \; . \qquad \ldots . (5.14)$$

(ii) The other approximation made compensates for the neglect of the boundary and the conditions imposed there. Since the temperature is now the same over the whole region, it follows that the temperature just inside the boundary is different from the temperature of the environment (or the temperature imposed on the boundary). So the first term in (11), which is proportional to the heat flux on the surface S, is replaced by a term which suggests a heat loss to the environment given by Newton's law of cooling. That is, $\frac{1}{S}\int_S \operatorname{grad}\theta . d\underset{\sim}{S} \approx -\beta\tilde{\theta}$, where S is the surface area of the region V. (The surroundings are assumed to be at zero temperature). The quantity β is called the effective heat-transfer coefficient. It is called this because the coefficient represents the surface cooling coefficient (see p.6), when the temperature variation across the region is replaced by an averaged temperature. The approximation which is made can be regarded as a truncated perturbation expansion also. For the expressions above to be equal, β would normally be a function of time. In fact

$$\beta(t) \quad = \quad \int_S \operatorname{grad}\theta . d\underset{\sim}{S} \; / S\tilde{\theta} \; . \qquad \qquad . \; . \; . \; . \; (5.15)$$

Since interest is focussed on times near those at which θ reaches its maximum, and conditions are quasi-steady, $\beta(t)$ is approximately constant. This is the approximation made here. (Note that when $t=0$, β must be infinite). Hence the equation can be written as

$$\frac{d\tilde{\theta}}{dt} + \frac{S}{V}\beta\tilde{\theta} = -a\frac{d\tilde{\lambda}}{dt} \; . . \qquad \qquad . \; . \; . \; . \; (5.16)$$

Thus the system has been reduced to the pair of ordinary differential equations (14) and (16) in t. The spatial variation of θ and λ has been eliminated, see Fig.5.4.

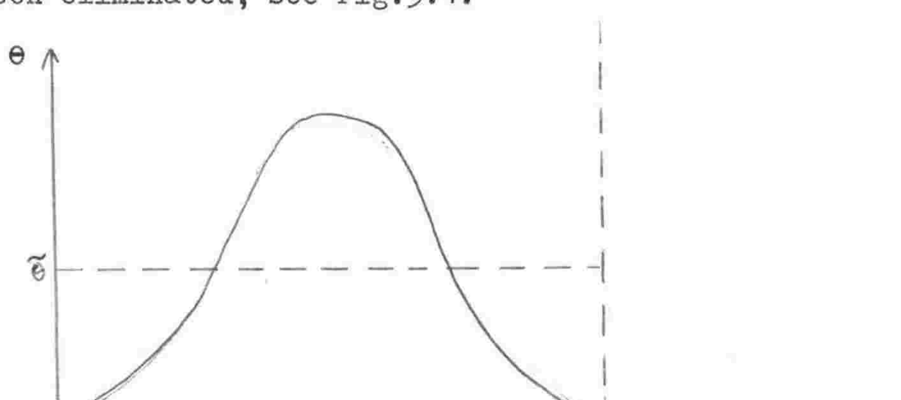


Fig.5.4.

The problem which arises is to determine this value of β for the different geometries discussed. Thomas et. al. were concerned with determining the conditions for "criticality" and so interest has been confined with times prior to the temperature reaching its maximum. For zero order reactions ($n=0$), Kamenetskii[1] obtained values from the heat balance (see equation (16)) in the steady state. To facilitate discussion of this, the quantities $\tilde{\theta}$ and $\tilde{\lambda}$ will be simply written as θ and λ, where it is now understood that the former are meant. Hence, in the steady state

$$f(\theta) = \frac{S}{V}\beta\theta \; . \qquad \qquad (5.17)$$

Kamenetskii, using a binomial approximation to the Arrhenius law, wrote $f(\theta) = \delta e^{\theta}$. Then, the steady state solution for the temperature is given by solving the resulting transcendental equation. In the cases mentioned before $S/V = 1+j$. This has two roots provided the parameter $(1+j)\beta$ is sufficiently large (see Fig.5.5).

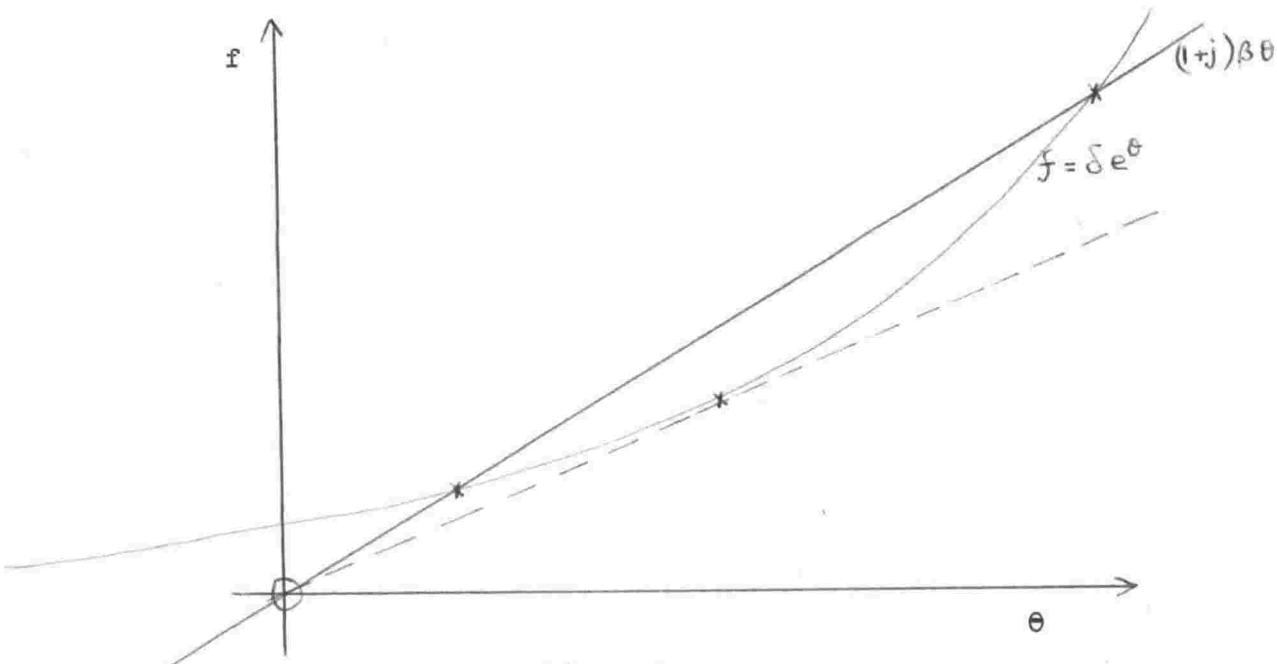


Fig.5.5.

The smallest value of β for which the equation has real roots represents the critical state (i.e. if β were smaller, then it is not possible to find a steady state solution, in fact the system is unstable). Hence, by finding the gradient of the tangent to $f = \delta e^{\theta}$ which passes through the origin it follows that $\beta = \delta e/(1+j)$.

Thomas[9] uses these estimates in determining the conditions for a critical state (in the sense that he formulated) for a reaction other than one of zero order. The validity of this depends on the extent to which the transient temperature distribution is of the same form as the critical steady state. Probably the latest paper of Adler and Enig[4] gives the most illustrative description of the system, that is equations (14) and (16). Here the equations are combined as

$$\frac{d\theta}{d\lambda} = -\frac{1}{a}\left(1 - A\theta/\lambda^{n} f(\theta)\right), \qquad \ldots . (5.18)$$

obtained by dividing the equations, where $A = (1+j)\beta$ and the initial conditions $\lambda = 1$, $\theta = 0$. t is regarded as a parameter for the integral curves obtained by integrating equation (18). These are illustrated below in Fig.5.6. (See over page).

From equation (12), the significant parameters are a and A. The rest of the paper is devoted to discussing the relationship between them when the conditions are critical i.e. to finding the first curve which passes through a point of inflection, and the corresponding maximum temperature rise. This is called by the ignition temperature by the chemists. The above analysis gives $\theta_{max} = 1 + n^{\frac{1}{2}}$. To the chemist this represents the highest temperature possible before another reaction takes over and ignites the material. The prevention of such uncontrolled combustion is responsible for much of the interest of this system among chemists.

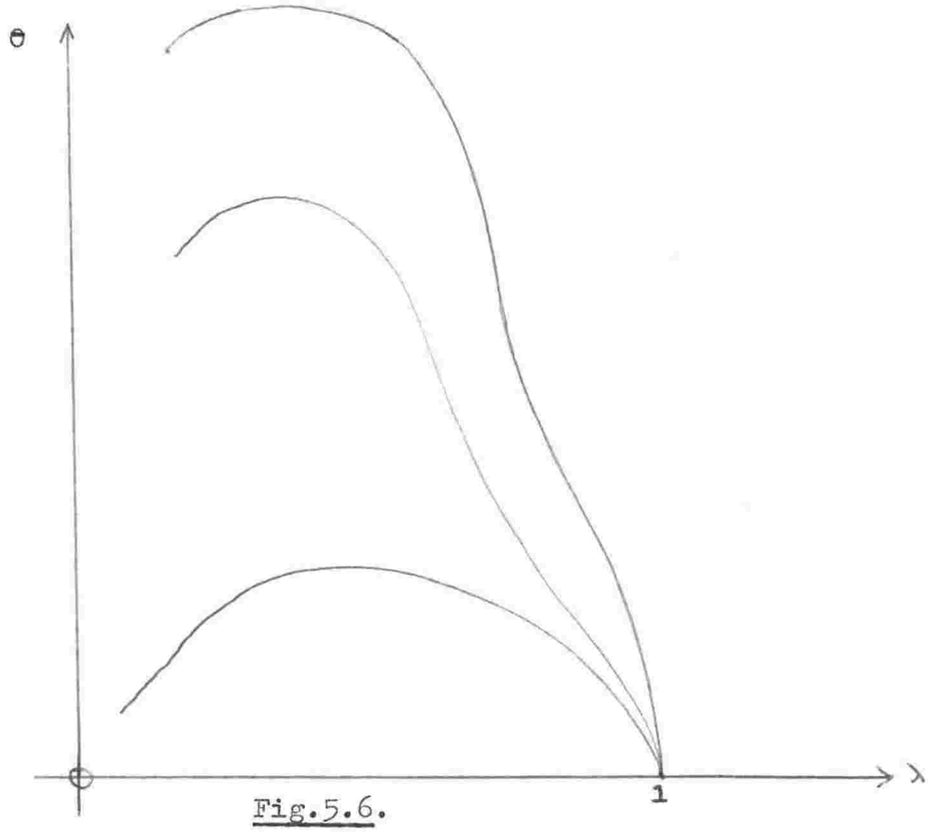


Fig.5.6.

It is felt that, if it/wished to use the criterion given by Thomas to classify reactions as stable or unstable, it would be much more useful to consider the asymptotic stability as discussed earlier. The introduction of the of the effective heat-transfer coefficient is reasonable, in that it will give a fairly accurate answer; provided the transient temperature distribution up to and near its maximum is nearly the same as in the critical steady state. However, it is not a technique that naturally lends itself to higher order approximations or that will allow the error made in the approximation to be calculated easily.

Chapter 6.

THE CUT-OFF PROBLEM

In this chapter, a detailed discussion of what will be called the cut-off problem will be given. It is felt that there is a class of problems which are of considerable mathematical interest and are in many ways like the classical free boundary problems in fluid dynamics.

6.1. The Existence of Cut-off.

It is intended to show that there is a class of problems for which the reactant is exhausted in a finite time. The time taken to exhaust the reactant will, of course, be a function of position and so there will appear a boundary, as yet unknown, beyond which no further heat is generated. It was shown in Chapter 2 (section 2.4) that there did exist a unique solution of this problem. Consider the coupled pair of equations

$$\Delta\theta + a\lambda^n f(x,\theta) = \frac{\partial\theta}{\partial t}, \qquad \ldots . (6.1)$$

$$\frac{\partial\lambda}{\partial t} = -\lambda^n f(x,\theta) . \qquad \ldots . (6.2)$$

It will be assumed that f is a bounded positive function. (As it was mentioned in Chapter 3, f is nondecreasing with θ also.) These requirements were all satisfied in the physical situations from which this analysis arose.

Equation (2) can be written

$$\frac{\partial}{\partial t}\left(\frac{\lambda^{1-n}}{n-1}\right) = f(x,\theta), \qquad n \neq 1 \qquad \ldots . (6.3)$$

$$\frac{\partial}{\partial t}(\log 1/\lambda) \quad = \quad f(x,\theta) \;, \qquad n = 1 \;. \qquad \ldots . (6.4)$$

In the first case, $n \neq 1$, if λ^{1-n} is plotted against time for a fixed x, the slope is given by $(n-1) f(x,\theta)$. Assume that the reactant is consumed in a finite time, i.e. $\lambda = 0$ for $t = t_o$. Then as t tends to t_o, λ^{1-n} tends to zero or infinity according as n is less than or greater than unity. This is illustrated below.

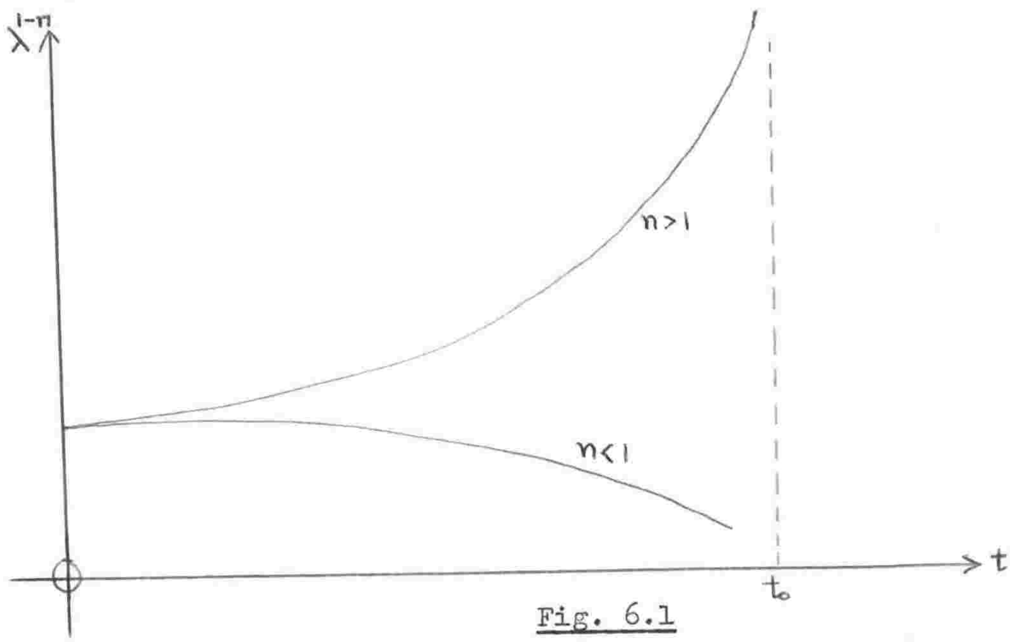


Fig. 6.1

Now, if a function of time is unbounded as t tends to t_o, then it follows that its derivative (assuming that it exists) is also unbounded as t tends to t_o. This is proved in the following lemma.

Lemma: Assume that $T(t)$, $T'(t)$ exist for $0 \leq t < t_o$ and that $T(t)$ is unbounded as $t \to t_o$. Then $T'(t)$ is also unbounded as $t \to t_o$.

Proof: Assume to the contrary that $T'(t)$ is bounded for all t, and in particular as $t \to t_o$. Then there exist B_1, B_2 such that $B_2 \leq T'(t) \leq B_1$,

$$\text{i.e.} \quad B_2 t \leq T(t) - T(0) \leq B_1 t \;,$$

which implies that $T(t)$ is bounded as $t \to t_o$; thus contradicting the proposition.

Hence, if $n > 1$, $f(x,\theta)$ tends to infinity as t tends to t_o. This contradicts the requirement that f be bounded. Further it follows that, in the case of $n > 1$, all the reactant cannot be consumed in a finite time. In the case of $n < 1$ it can be shown that the reactant will be consumed in a finite time. Since f is bounded and positive

$$M \geqslant f(x,\theta(x,t)) \geqslant m \qquad \text{for all } x,t.$$

Thus from (3) it follows that

$$\frac{\partial}{\partial t}(\lambda^{1-n}) \leqslant (n-1)m , \qquad (n < 1)$$

i.e. $$\lambda^{1-n} \leqslant \lambda_o^{\,1-n} - (1-n)mt , \qquad \ldots . (6.5)$$

where λ_o is the initial concentration of λ as a function of position. However, since it is an obvious physical requirement that λ remain positive, it follows that λ becomes zero in a finite time, say t_o. Then for $t > t_o$ there is no further heat generation and equation (1) becomes simply

$$\Delta\theta = \frac{\partial\theta}{\partial t} , \qquad \ldots . (6.6)$$

which is the heat conduction equation with no heat source.

For the case $n = 1$, plot $\log(1/\lambda)$ against time and note that $\log(1/\lambda)$ tends to infinity as λ tends to zero.

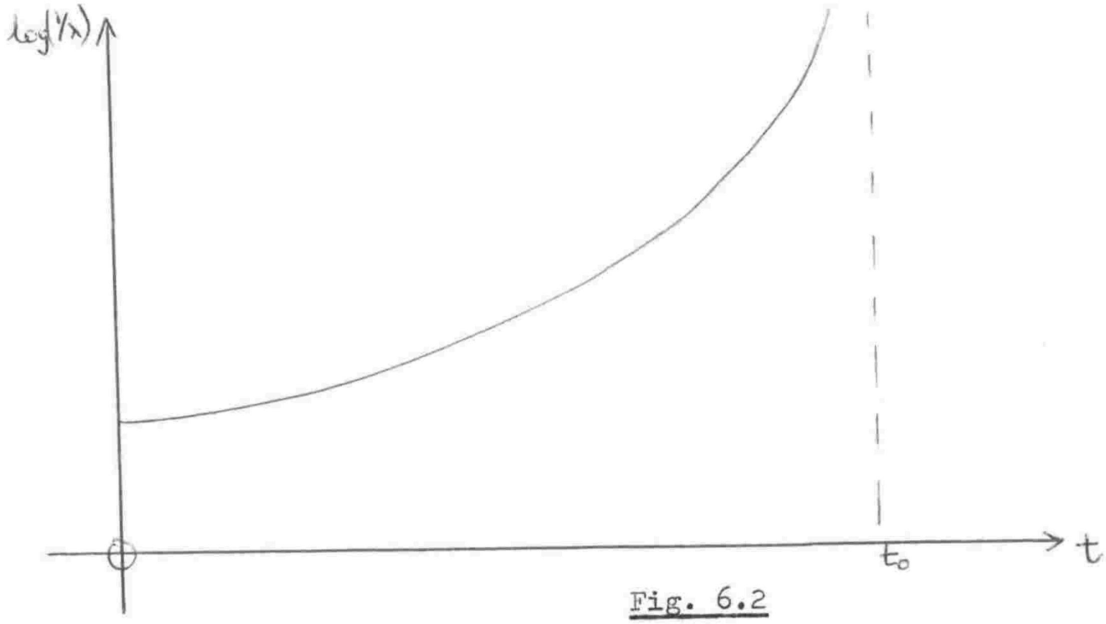


Fig. 6.2

The slope will be given by $f(x,\theta)$. Hence the same argument will apply as it did in the case $n > 1$.

Thus it may be concluded:

$n < 1$ the reactant will be consumed in a finite time,

$n \geqslant 1$ the reactant cannot be consumed in a finite time and will tend asymptotically to zero as t becomes large. This phenomenon (in the former case) has prompted the name "cut-off problem".

When there is no cut-off ($n \geqslant 1$) the problem of actually solving the equations (1) and (2) will be more straight-forward, in that, although the equations are nonlinear, there is no division of the region in the (x,t) space in which they apply.

Interest will now be confined to $n < 1$, where there is a cut-off time t_o which will, in general, be a function of x, say $C(x)$. The problem may be stated as

$$\Delta\theta + a\lambda^n f(x,\theta) = \frac{\partial\theta}{\partial t}, \quad t < C(x) \qquad \ldots . (6.7)$$

$$\Delta\theta = \frac{\partial\theta}{\partial t}, \quad t > C(x) \qquad \ldots . (6.8)$$

$$\frac{\partial \lambda}{\partial t} \quad = \quad - \lambda^n f(x,\theta) \quad . \qquad . \ . \ . \ . \ (6.9)$$

(The last of these is subject to the condition $\lambda = 0$ when $t = C(x)$). These equations are to be solved with given initial (θ and λ) and boundary (θ only) conditions. If n is zero, the interpretation that $f = 0$ when $t > C(x)$ must be added. This will mean a sharp cut-off in the heat source and rate of reactant consumption. There are also some continuity conditions on $t = C(x)$. It was shown in Chapter 2 that the temperature and its first derivatives with respect to x_i are continuous on the cut-off surface. Physically this is merely asserting that both the temperature and heat flux are continuous. Note that it is assumed here that there is no change in the thermal properties of the material brought about by this burning process. Otherwise these conditions (and the equations) would have to be modified to allow for this.

In the case of a nonzero order reaction it has been shown that $\partial\theta/\partial t$ is continuous on $t = C(x)$. Further it was noted that in a reaction of zero order it is not possible, in general, to attribute the discontinuity on $t = C(x)$ wholly to either $\partial\theta/\partial t$ or to the second derivatives of θ with respect to the x_i. Though in the special case of $C(x)$ constant it is only $\partial\theta/\partial t$ which can be discontinuous.

To illustrate the position further, consider the semi-infinite problem $x > 0$ in which the temperature is prescribed on $x = 0$ (and when $t = 0$). Then the cut-off curve (as it is in this case) divides the positive quadrant of the (x,t) plane as it is shown in Fig.6.3.

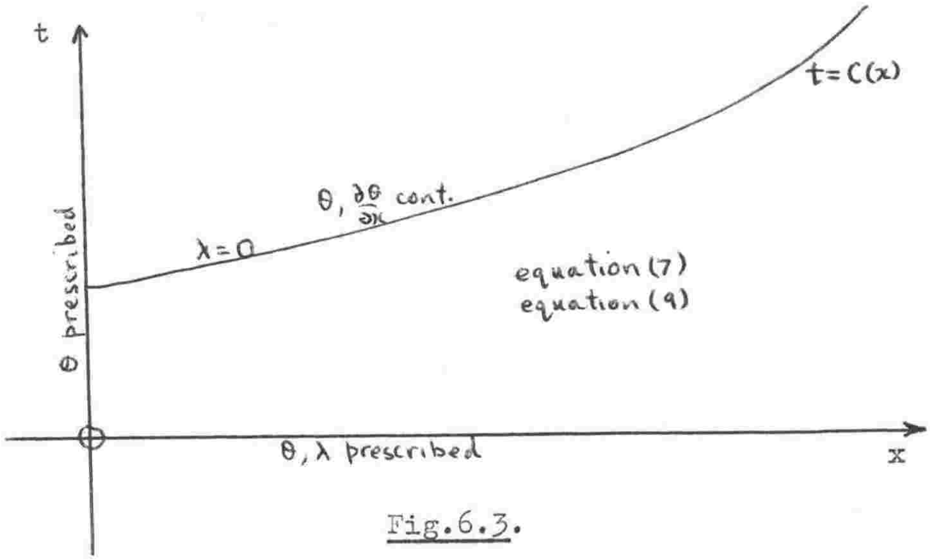


Fig.6.3.

As it is drawn with $C'(x) > 0$, the cut-off curve represents a wave advancing into the region leaving behind it a burnt out residue in which the ordinary heat conduction equation applies. In the solution of these problems one of the primary unknowns is, of course, the cut-off curve itself, as well as the dependent variables θ and λ. The problem is still well-posed however, because of the information about λ on $t = C(x)$.

6.2. Examples of Cut-off Problems.

Consider the zero order reaction in which f is merely a function of θ. Then the cut-off problem when the equations are independent of x, is given by

$$\frac{d\theta}{dt} = af(\theta) = -a\frac{d\lambda}{dt}, \qquad t < C. \qquad \ldots . (6.10)$$

This is a comparatively simple system to solve, at least in principle. For example, when $f(\theta) = \alpha + \beta\theta$ the solution subject to $\theta = 0$, $\lambda = 1$ at $t = 0$, is $\theta = \frac{\alpha}{\beta}(e^{a\beta t} - 1)$, $\lambda = 1 - \frac{\alpha}{a\beta}(e^{a\beta t} - 1)$. The time of cut-off is given by $\lambda = 0$ i.e. $C = \frac{1}{a\beta}\log\left(1 + \frac{a\beta}{\alpha}\right)$. Hence $d\theta/dt = 0$ for $t > C$, which implies that $\theta = a$, and $\lambda = 0$ for $t > C$. These are illustrated below.

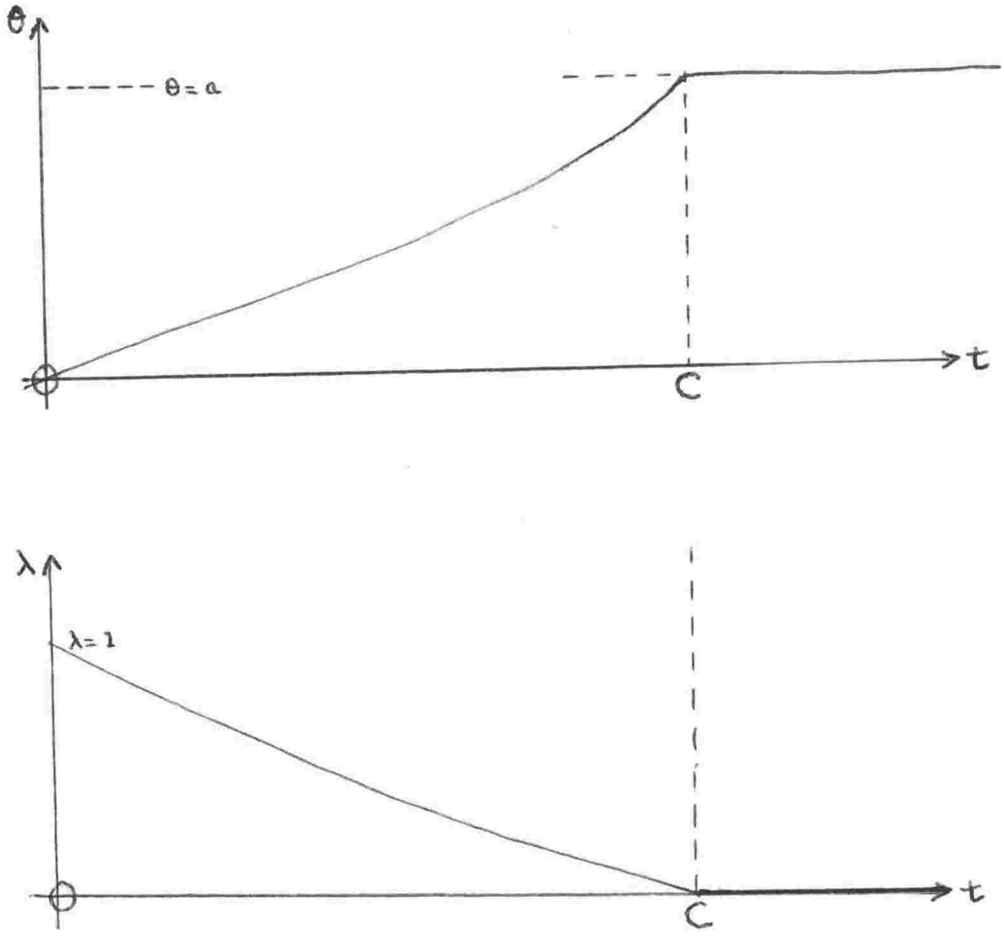


Fig. 6.4

The solution above would be the asymptotic value as x tends to infinity of the semi-infinite problem with $\theta = 0$ on $x = 0$. This problem is more difficult to solve. That is, it is required to solve

$$\frac{\partial^2\theta}{\partial x^2} + a(\alpha + \beta\theta) = \frac{\partial\theta}{\partial t}, \quad t < C(x) \qquad \ldots . (6.11)$$

$$\frac{\partial^2\theta}{\partial x^2} = \frac{\partial\theta}{\partial t}, \quad t > C(x) \qquad \dots . (6.12)$$

$$\frac{\partial\lambda}{\partial t} = -(\alpha + \beta\theta), \quad t < C(x) \qquad \dots . (6.13)$$

subject to $\theta = 0$ on $x = 0$ and when $t = 0$; $\lambda = 1$ when $t = 0$, $\lambda = 0$ on $t = C(x)$. For $\beta > 0$ the cut-off curve will appear as shown below, having a horizontal asymptote $t = C$ as above.

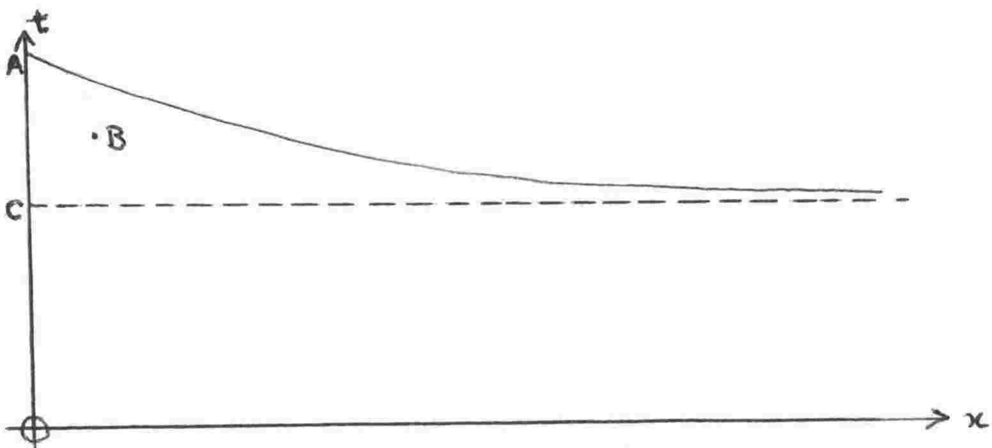


Fig. 6.5.

The solution of (11) is easily obtained for $t < C = \min_{x>0} C(x)$, by taking Laplace transforms, as $\theta = \alpha \int_0^t e^{\beta u} \operatorname{erf}(x/2u^{\frac{1}{2}})\, du$. However, it does not appear possible to use any such technique for points for which $t > C$. For example, at the point B (x_B, t_B), the solution must in some way take into account the fact that the reactant has been burnt out already at some points.

At this stage of the problem, it was considered that one way of obtaining the solution would be to use a perturbation expansion in β. For when $\beta = 0$, the cut-off curve is t = constant (passing through A in Fig. 6.5). Denote this by $t = C_0$. Substitute $\theta = \theta_0 + \beta\theta_1 + \dots$, $\lambda = \lambda_0 + \beta\lambda_1 + \dots$. And further it was thought that the continuity conditions on $t = C(x)$ could be transferred to $t = C_0$ by using suitable

Taylor expansions. However, when this was done it was noticed that the expansions were singular. On closer inspection of the problem it is found that this should have been expected, for, the zero order problem has as cut-off curve a characteristic of the parabolic differential equation. So the solution so obtained was not in fact taking into account what it should have been, i.e. that the reactant is exhausted at some points earlier than it is at others. This technique would have worked for the solution independent of x i.e. as in equation (10). Here θ and λ could have been expanded in power series in β; the solution obtained being exactly as given, except that it would be expanded in powers of β. This is, of course, because the cut-off curve, for any β, occurs at the same time for any point.

The problem discussed above has not been solved completely, however, it is hoped that it serves to illustrate some of the properties of the system. It is now intended to discuss in detail another problem of interest, which can be solved using a similarity technique.

6.3. A Similarity Solution.

This problem, is again a zero order reaction, which as shown in section 1, will exhaust the reactant in a finite time. Heat will be generated according to $f = \alpha + \beta\theta/x^2$. Hence the problem can be stated

$$\frac{\partial^2\theta}{\partial x^2} + \alpha + \frac{\beta\theta}{x^2} = \frac{\partial\theta}{\partial t}, \qquad t < C(x) \qquad \ldots . (6.14)$$

$$\frac{\partial^2\theta}{\partial x^2} = \frac{\partial\theta}{\partial t}, \qquad t > C(x) \qquad \ldots . (6.15)$$

$$\left.\begin{aligned} \frac{\partial\lambda}{\partial t} &= -\,(\,\alpha + \beta\theta/x^2\,) \\ \text{subject to } &= 0 \text{ on } t = C(x). \end{aligned}\right\} \qquad \ldots . (6.16)$$

There will be solved subject to the initial conditions $\theta = ax^2$, $\lambda = \gamma x^2$ and boundary condition $\theta = bt$ on $x = 0$. It is possible to eliminate one of the constants. By a suitable sealing of the dependent variables, it follows that α can be taken as unity. This can be done by writing $\alpha\theta$ and $\alpha\lambda$ for θ and λ respectively, and redefining a and b as αa and αb, the equations and boundary conditions are then as above; with $\alpha = 1$. In effect all this is doing, is choosing a particular member of a class of problems, which are defined for various α. The particular member is that obtained when $\alpha = 1$. On first glance, it appears that this problem possesses all the difficulties of the one in the previous section. However, this problem possesses a similarity solution which enables the partial differential equations to be written as ordinary differential equations in a single variable. For if the transformations

$$\begin{aligned} x &\longrightarrow rx \\ t &\longrightarrow r^2 t \\ \theta &\longrightarrow r^2\theta \\ \lambda &\longrightarrow r^2\lambda, \end{aligned}$$

are applied to both the equations and the boundary conditions these are <u>unchanged</u>. Hence the problem can be written in terms of the single variable $z = x/t^{\frac{1}{2}}$. Define

$$\left.\begin{aligned} \theta &= x^2 g(z), \\ \lambda &= x^2 h(z). \end{aligned}\right\} \qquad \ldots . (6.17)$$

Then equation (16) reduces to

$$\frac{1}{2}h'(z) = \frac{1}{z^2} + \frac{\beta g(z)}{z^3} , \qquad . . . . (6.18)$$

$\frac{1}{z^3}$

subject to the condition that h tends to γ as z tends to infinity. The cut-off curve in the x,t plane is defined by $\lambda(x,t) = 0$, i.e. $h(z) = 0$, which implies $z = K$. Hence the curve $t = C(x)$ will be the parabola, $x = Kt^{\frac{1}{2}}$. Equation (18) is applicable for only $z > K$ and is subject to the defining condition for K, $h(K) = 0$.

Likewise equations (14) and (15) reduce to

$$z^2g''(z) + (4z + z^3/2)g'(z) + (\beta + 2)g(z) + 1 = 0, \; z > K \quad ...(6.19)$$

$$z^2g''(z) + (4z + z^3/2)g'(z) + 2g(z) = 0, \; z < K \quad ...(6.20)$$

The matching conditions on the cut-off curve $z = K$ become simply g and dg/dz continuous on $z = K$.

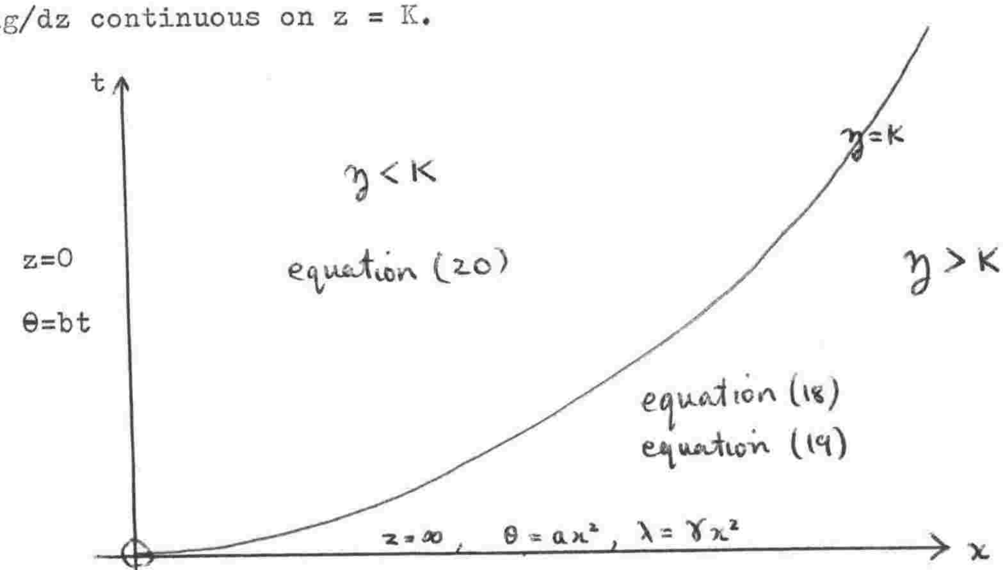


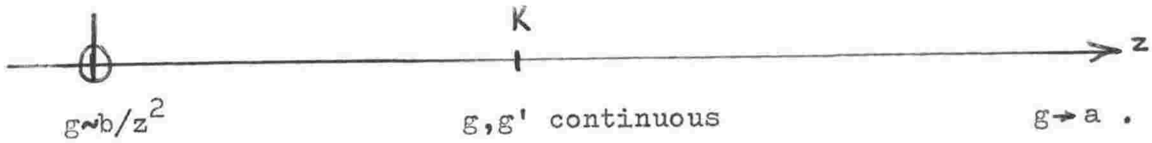
Fig.6.6.

The boundary and initial conditions on θ and λ can now be applied to g and h respectively. Hence,

$$\left.\begin{array}{l} g \rightarrow a \\ h \rightarrow \gamma \end{array}\right\} \text{ as } z \rightarrow \infty$$

$$g \sim b/z^2 \text{ as } z \rightarrow 0, \qquad \text{i.e. } z^2g(z) \rightarrow b \text{ as } z \rightarrow 0.$$

On looking at the z plane for z from zero to infinity, the situation is as



Since the function g depends on z alone, it follows that the isotherms (lines joining points of the same function value) are parabolas in the x,t plane also.

Equation (20) can be solved by letting $g(z) = w(z)/z^2$ and so

$$w'' + zw'/2 - w = 0, \qquad w(0) = b. \qquad \ldots\ldots (6.21)$$

One solution of this differential equation is $1 + z^2/2$ and so the other can be found by substituting $w = (1 + z^2/2)v(z)$ in (21). On substituting, and solving for w, and hence g, it follows that

$$g(z) = b(\tfrac{1}{2} + 1/z^2) + R\left(e^{-z^2/4}/z + \pi^{\frac{1}{2}}(\tfrac{1}{2} + 1/z^2)\operatorname{erf}(z/2)\right), \qquad \ldots\ldots (6.22)$$

where R is an arbitrary constant. The latter will be found, of course, by using the matching conditions at z = K. In general, R will be a function of K.

However, equation (19) presents some difficulty. By writing $y = 1/z$ it follows that

$$y^2g'' - (2y + 1/2y)g' + (\beta + 2)g + 1 = 0. \qquad \ldots\ldots (6.23)$$

Hence it follows that $y = 0$ (i.e. $z = \infty$) is an irregular singular point and so there will not exist a solution in series. Further the solution of (19) when $\beta = 0$ (c.f.(22)) is

$$g_o = -\tfrac{1}{2} + P(\tfrac{1}{2} + 1/z^2) + Q\left(e^{-z^2/4}/z + \pi^{\frac{1}{2}}(\tfrac{1}{2} + 1/z^2)\operatorname{erf}(z/2)\right).$$

That is $g_o(\infty)$ is finite. Then it would be expected that $g(\infty)$ is finite also, since $\beta \neq 0$ does not alter greatly the character of the differential equation. The complementary function of (19) is found by letting

$$g(z) = s^{\delta} G(s), \qquad \dots \dots (6.24)$$

where $s = z^2$ and δ is a constant. Hence $G(s)$ satisfies

$$4sG'' + (8\delta + 10 + s)G' + \delta G = 0, \qquad \dots \dots (6.25)$$

provided $4\delta^2 + 6\delta + \beta + 2 = 0$. The differential equation in (25) can be solved by taking a contour integral

$$G(s) = \int_C e^{rs} P(r)\, dr,$$

where C is an appropriate contour in the complex plane. This gives

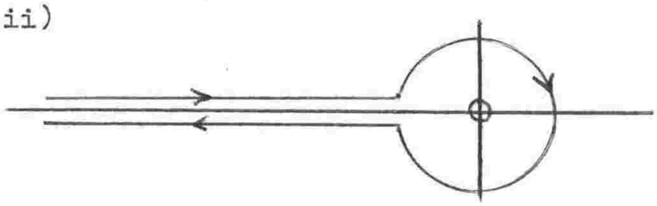
$$\left.\begin{aligned} G(s) &= \int_C e^{rs}\, r^{\delta-1}(r+1/4)^{\delta+3/2}\, dr, \\ \text{where } C \text{ is such that } &\Big[e^{rs}\, r^{\delta}(r+1/4)^{\delta+5/2} \Big]_C = 0. \end{aligned}\right\} \quad \dots (6.26)$$

Since δ must satisfy only the quadratic equation above, then it can be chosen as the positive root, which implies $-3/4 \leqslant \text{Real}(\delta) \leqslant -\frac{1}{2}$, provided $\beta \geqslant 0$.

Two possible choices for C are:

(i) $(-\infty, -1/4)$,

(ii)



.

Thus the two independent solutions for $G(s)$ are

$$\int_0^\infty e^{-rs}\left\{(1/4 - r)^{\delta+3/2} - (1/4)^{\delta+3/2}\right\} r^{\delta-1}\, dr , \quad \text{and}$$

$$\int_{1/4}^\infty e^{-rs}(1/4 - r)^{\delta+3/2}\, r^{\delta-1}\, dr ,$$

where $s = z^2$ and δ is the root of $4\delta^2 + 6\delta + \beta + 2 = 0$ which has the greater real part.

After a little manipulation these can be written as

$$I_1(z,\beta) = \frac{1}{\delta z^{4\delta+3}} \int_0^\infty e^{-s}\left\{(z^2/4 - s)^{\delta+3/2} + (\delta + 3/2)(z^2/4 - s)^{\delta+\frac{1}{2}}\right\} s^\delta ds, \quad \ldots . (6.27)$$

$$I_2(z,\beta) = \frac{1}{z^{4\delta+3}} \int_{z^2/4}^\infty e^{-s} (z^2/4 - s)^{\delta+3/2} s^{\delta-1} ds . \quad \ldots . (6.28)$$

Thus the solution of (19) can be written as

$$g(z) = z^{2\delta}\left\{C\, I_1(z,\beta) + D\, I_2(z,\beta)\right\} - \frac{1}{\beta+2}, \quad \ldots . (6.29)$$

where C and D are arbitrary constants. Since equation (20) is the same as that satisfied by the complementary function of (19) when β is set equal to zero, then the general solution of the former is (compare (29)):

$$g(z) = z^{2\delta_0}\left\{A\, I_1(z,0) + B\, I_2(z,0)\right\}, \quad \ldots . (6.30)$$

where $\delta_0 = \delta$ when $\beta = 0$ i.e. δ_0 is the larger root of $4p^2 + 6p + 2 = 0$, which means that $\delta_0 = -\frac{1}{2}$. It is a simple exercise to verify that both $I_1(z,0)$ and $I_2(z,0)$ are linear combinations of the linearly independent solutions given in (22). In fact, it can be shown that they both behave like $-\pi^{\frac{1}{2}}/z$ as z tends to zero. Then in order to satisfy the requirement for g(z) as z 0, it follows that $A+B = -b/\pi^{\frac{1}{2}}$.

Now as $z \to \infty$, $g(z) \to a$, and so the asymptotic behaviour of the integrals in (27) and (28) must be calculated. It can be shown that for z large,

$$\left.\begin{aligned} z^{2\delta} I_1(z,\beta) &\longrightarrow \left(\tfrac{1}{4}\right)^{\delta+3/2} \Gamma(1+\delta)/\delta \\ z^{2\delta} I_2(z,\beta) &\longrightarrow 0 \end{aligned}\right\} \text{ as } z \to \infty . \quad . . (6.31)$$

$$\text{Hence, } C = \left(a + \frac{1}{\beta+2}\right)\frac{\delta 4^{\delta+3/2}}{\Gamma(1+\delta)} . \quad \ldots . (6.32)$$

Thus the solution of the equations (19) and (20) can be stated,

$$g(z) = -z^{-1}\{b\,I_1(z,0)/\pi^{\frac{1}{2}} + B(K)(I_1(z,0) - I_2(z,0))\}\ , \quad z < K \quad \ldots (6.33)$$

$$g(z) = z^{2\delta}\left\{(a + \frac{1}{\beta+2})\frac{\delta 4^{\delta+3/2}}{\Gamma(\delta+1)}\ I_1(z,\beta) + D(K)\,I_2(z,\beta)\right\} - \frac{1}{\beta+2}\ , \quad z > K \quad \ldots\ldots (6.34)$$

where B,D are functions of K given by the conditions; g and dg/dz are continuous on z = K. All the way through this computation the known expression for $z < K$ (see equation (22)) was of assistance in checking the solutions obtained.

The quantity K , as mentioned previously, is given by h(K) = 0. By integration of equation (18) , using (19), it follows that K satisfies the following equation

$$\frac{12}{K^2} + \beta g(K)(1 + 10/K^2) + 2\beta g'(K) - a\beta - \gamma(12 + \beta) = 0. \qquad (6.35)$$

Hence, using (35) and the equations obtained from (33) and (34) for g and dg/dz continuous on z=K, it is possible to find the complete answer to the problem. However, the resulting equation for K is extremely difficult to use in practice. The author has actually found this equation, but it will not be written here. In order to demonstrate the type of equations obtained, the asymptotic value of K will be obtained for K large. This can easily be done using the asymptotic behaviour of the integrals given in (31) and (32). Thus using the expressions in (33) and (34) at z = K, for z large it follows that,

$$B \sim (2a-b)\tfrac{1}{2}\pi^{\frac{1}{2}} \quad \text{for K large.} \qquad \ldots\ldots (6.36)$$

Then this may be used in the equation for K, i.e. (35). However, in in using asymptotic expansions of I_1 and I_2, care must be taken with the respective orders of magnitude. For, using (36),

$$\left.\begin{aligned} g(K) &= a(1+2/z^2) - \ldots, \\ g'(K) &= -4a/z^3 - \ldots \,. \end{aligned}\right\} \quad \text{for large } z \,. \qquad \ldots. \quad \begin{matrix}(6.37)\\(6.38)\end{matrix}$$

If just the first order terms are taken it follows that

$$\frac{12}{K^2} + a\beta(1+10/K^2) - a\beta - \gamma(12 + \beta) = 0,$$

$$\text{i.e.} \quad K = \left(\frac{12 + 10a\beta}{\gamma\,(12+\beta)}\right)^{\frac{1}{2}} \quad \text{for } K \text{ large.} \qquad \ldots. \quad (6,39)$$

This expression represents the first approximation to the behaviour of K for small γ. By taking higher order terms a better approximation could be obtained. Likewise the behaviour of K with β can be obtained by finding asymptotic expansions of I_1 and I_2 for large β. It would be expected that β large would imply that **K** is large also.

Hence it can be seen that it is possible to use the equations to obtain estimates for K. Of course, it is possible in the general case, but this would involve an enormous amount of calculation.

Chapter 7.

CONCLUSIONS

It is felt that the most interesting features of the system described in this thesis have been discussed. This is both from the point of view of previous investigations into the problem, and of that of the mathematician. With reference to the aspects discussed in Chapters 2 and 3, it is hoped that as our knowledge and scope of the machinery necessary to establish the existence, uniqueness, etc. of solutions expands, so will the generality of the results obtained. There is, of course, a lot of interest in these qualitative properties at present and no doubt some significant advances will be made in the near future. It is felt that there is a more general comparison theorem possible, which would have embodied the results given in Chapter 3.

From the technical point of view there are, of course, a lot of difficult problems to solve with this system. Many of the problems for which it is possible to obtain solutions analytically are given in the book by Carslaw and Jaeger[22]. However, there is a much greater number of problems for which there is no such solution. For these, one is forced to make various approximations and find perturbation expansions in different regions of the independent variables. By doing this, one often gains an insight into the difficult features of such problems. This is usually of assistance when the problem is to be computed on an electronic computer. With the tremendous developments in computing, it is now possible to solve many of the extremely nonlinear problems which were too formidable in the past. This approach is the one which will usually be the most fruitful for the practising scientist. However, this has not been attempted here.

There are many aspects of this problem that have not been considered. As it has been mentioned in the context of this thesis, there are many simplifying assumptions which have been made to the physical model from which this analysis arose. Probably the most obvious of these is the one that supposed the thermal properties of the medium are unchanged by the combustion. Some of the required machinery for proving the existence of a solution to such a system has been covered in Chapter 2, and this would form an interesting generalization of the results.

APPENDIX

A.1. Existence of Solutions to $L(\theta)=\eta(x,t,\theta)$.

Assume S_T belongs to C^2 and $C^{2+\alpha}$, L satisfies the conditions I and II (as in Chapter 2), and $\eta(x,t,\theta)$ is Hölder continuous (exponent α) in $\bar{D}_T$ for each fixed value of θ. Further assume that η satisfies a Lipschitz condition in θ, with Lipschitz constant M; and that there exists two functions $\underline{\theta}$ and $\bar{\theta}$ satisfying the inequalities given in (2.15). Finally assume that there exists a function ψ of class $C^{2+\alpha}$ in $\bar{D}_T$ which coincides with the given boundary conditions $\theta_o(x,t)$ on S_T and on $\bar{B}$ at $t = 0$. Then there exists a solution of the system

$$\begin{aligned} L(\theta) &= \eta(x,t,\theta), \\ \theta &= \theta_o(x,t) \text{ on } S_T \text{ and on } \bar{B} \text{ at } t = 0, \end{aligned}$$

such that θ is of class $C^{1+\beta}$ in D_T for any $0<\beta<1$ and of class $C^{2+\gamma}$ for some $\gamma>0$.

<u>Proof</u>: Consider the set of functions defined by

$$\begin{aligned} L(\theta_1) - M\theta_1 &= \eta(x,t,\bar{\theta}) - M\bar{\theta} , \\ L(\theta_n) - M\theta_n &= \eta(x,t,\theta_{n-1}) - M\theta_{n-1} \quad \text{for } n=2,3,\dots ; \\ \theta_n &= \theta_o(x,t) \text{ on } S_T \text{ and on } \bar{B} \text{ at } t = 0,\ n\geq 1. \end{aligned}$$

Now if θ_{n-1} is Holder continuous with exponent α in $\bar{D}_T$, then so is the function $\phi_{n-1}(x,t) \equiv \eta(x,t,\theta_{n-1}(x,t))$. Then by Theorem 2 θ_n exists and is Hölder continuous with exponent α in $\bar{D}_T$. Furthermore, from Theorem 3, for any $0\leq\delta<1$

$$|\theta_n|_{1+\delta} \leq P(|\eta_{n-1}|_o + |\psi|_2 + M|\theta_{n-1}|_o).$$

It is shown in McNabb[10] that

$$\underline{\theta} \leq \theta_n \leq \theta_{n-1} \leq \overline{\theta},$$

that is (θ_n) is a monotone decreasing sequence which is bounded below. This implies that $\phi_n(x,t)$ is also bounded in $\overline{D}_T$ and so $|\theta_n|_{1+\delta}$ is bounded by a constant P' independent of n.

Hence the limit of this sequence exists and defines a function θ in D_T. Further θ is Holder continuous of exponent δ. From Theorem 2, this means that the system

$L(\theta') - M\theta' = \eta(x,t,\theta) - M\theta$, $\theta' = \theta_o$ on the boundaries; has a solution θ' of class $C^{1+\beta}$ in D_T for any $0 < \beta < 1$ and of class $C^{2+\gamma}$ for some $\gamma > 0$.

Now

$$L(\theta' - \theta_n) - M(\theta' - \theta_n) = \phi(x,t) \equiv$$

$$\equiv \eta(x,t,\theta) - \eta(x,t,\theta_{n-1}) - M(\theta - \theta_{n-1})$$

and $\theta' - \theta_n = 0$ on the boundaries of D_T while

$$|\phi(x,t)| \leq 2M|\theta - \theta n{-}1| \quad \text{in } \overline{D}_T .$$

Since, by Theorem 3, $|\theta' - \theta_n| \leq K'|\phi(x,t)|$ and the righthand side tends to zero as n tends to infinity, θ' coincides with θ in $\overline{D}_T$. Hence this θ is the solution of the system as required, and is of class $C^{1+\beta}$ in D_T for any $0 < \beta < 1$ and of class $C^{2+\gamma}$ for some $\gamma > 0$.

Moreover, since each θ_n is bounded, it follows from the $1+\delta$ estimate above that

$|\theta|_{1+\delta} \leq P'$, where P' is dependent on only $\delta, L, \psi,$ and η.

A.2. Existence of Solution to the Complete System.

Assume S_T belongs to C^2 and $C^{2+\alpha}$, L satisfies the conditions I and II, as in Chapter 2, f and g satisfy the Lipschitz conditions given in (2.12) and (2.13), and g is negative for $\lambda \geqslant 0$ and zero when $\lambda = 0$. It is further assumed that there exists a function ψ of class $C^{2+\alpha}$ in $\bar{D}_T$ which coincides with the boundary conditions θ_o of θ on S_T and $\bar{B}$ at $t = 0$. Also the initial condition $\lambda_o(x,0)$ is assumed to be of class C^1 on $\bar{B}$, and it is assumed that there exists two functions $\underline{\theta}$ and $\bar{\theta}$ continuous in $\bar{D}_T$ and having continuous bounded derivatives in D_T, such that for $0 \leqslant \lambda \leqslant \lambda_o$,

$$L(\underline{\theta}) - f(x,t,\underline{\theta},\lambda) \geqslant 0 \geqslant L(\bar{\theta}) - f(x,t,\bar{\theta},\lambda),$$

$$\underline{\theta} \leqslant \theta_o \leqslant \bar{\theta} \quad \text{on } S_T \text{ and on } \bar{B} \text{ at } t = 0.$$

Then there exists a solution of the system

$$L(\theta) = f(x,t,\theta,\lambda),$$

$$\frac{\partial\lambda}{\partial t} = g(x,t,\theta,\lambda),$$

$$\theta = \theta_o(x,t) \text{ on } S_T \text{ and on } \bar{B} \text{ at } t = 0,$$

$$\lambda = \lambda_o(x,\theta) \text{ on } \bar{B} \text{ at } t = 0,$$

such that θ is of class $C^{1+\beta}$ in D_T for any $0 < \beta < 1$ and of class $C^{2+\gamma}$ in $\bar{D}_T$ for some $\gamma > 0$, and λ is of class C^1 in $\bar{D}_T$.

Proof: Consider the set of functions defined by

$$\frac{\partial\lambda_1}{\partial t} = g(x,t,\bar{\theta}, \lambda_1),$$

$$L(\theta_n) = f(x,t,\theta_n, \lambda_n), \qquad n=1,2,\ldots$$

$$\frac{\partial\lambda_n}{\partial t} = g(x,t,\theta_{n-1}, \lambda_n), \qquad n \geqslant 2$$

in D_T, where

$$\theta_n = \theta_o \quad (n \geqslant 1) \text{ on } S_T \text{ and on } \overline{B} \text{ at } t = 0,$$

$$\lambda_n = \lambda_o \quad (n \geqslant 1) \text{ on } \overline{B} \text{ at } t = 0.$$

Now if λ_n is Hölder continuous with exponent α in $\overline{D}_T$, then so is the function $f_n(x,t,\theta) \equiv f(x,t,\theta,\lambda_n(x,t))$. By the result in Appendix 1, θ_n exists and is certainly of class C^1 in $\overline{D}_T$. Moreover $|\theta_n|_{1+\delta} \leqslant P'$,

where P' depends on δ, L,ψ, and f_n. This means that P' depends on θ_n,λ_n, but as it will be shown that these are uniformly bounded it follows that there will exist a uniform bound for the sequence $(|\theta_n|_{1+\delta})$. In fact it can be shown that

$$\underline{\theta} \leqslant \theta_n \leqslant \overline{\theta} \quad \text{for each } n, \text{in } \overline{D}_T.$$

Theorem 4 implies that $\lambda_n(x,t)$ exists and, provided θ_{n-1} is of class C^1 in $\overline{D}_T$, then so too is λ_n. From the requirements on g it follows that each λ_n satisfies $0 \leqslant \lambda_n \leqslant \lambda_o$ in $\overline{D}_T$. Next it is shown that $\underline{\theta} \leqslant \theta_n \leqslant \overline{\theta}$ in $\overline{D}_T$. This follows from the comparison theorems proved by McNabb[10]. For

$$L(\theta_n) - f(x,t,\theta_n,\lambda_n) = 0 \leqslant L(\underline{\theta}) - f(x,t,\underline{\theta},\lambda_n),$$

$$L(\theta_n) - f(x,t,\theta_n,\lambda_n) = 0 \geqslant L(\overline{\theta}) - f(x,t,\overline{\theta},\ _n).$$

And since $\underline{\theta} \leqslant \theta_n \leqslant \overline{\theta}$ on the boundaries of D_T, these inequalities also hold in the interior. Also since each θ_n is Hölder continuous of exponent α (at least), then obviously each θ_n is equicontinuous on $\overline{D}_T$. By the Ascoli lemma, there exists a subsequence (θ_{n_k}), defined for k= 1,2,.., of (θ_n), converging uniformly to a limit function θ defined on $\overline{D}_T$. It is simple to show from $|\theta|_{1+\delta} \leqslant P'$ that θ is of class C^δ in $\overline{D}_T$, and further that θ is of class C^1 in x.

Likewise the same procedure follows from $0 \leq \lambda_n \leq \lambda_o$ which implies the existence of a limit λ. This limit is shown to be of class C^1 in $\overline{D}_T$, Each λ_n is of class C^1 in $\overline{D}_T$, where

$$\frac{\partial \lambda_n}{\partial t} = g(x,t,\theta_{n-1},\lambda_n).$$

Denote $h_n(t) \equiv \lambda_n(x,t) - \lambda_n(x',t)$. Therefore,

$$\frac{\partial h_n}{\partial t} = g(x,t,\theta_{n-1}(x,t),\lambda_n(x,t)) - g(x',t,\theta_{n-1}(x',t),\lambda_n(x',t)),$$

$$\text{i.e.} \left|\frac{\partial h_n}{\partial t}\right| \leqq M\left\{|h_n| + |\theta_{n-1}(x,t) - \theta_{n-1}(x',t)|\right\} + K|x - x'|,$$

using the Lipschitz condition on g. Note Mand K are independent of n. Then since each θ_{n-1} is of class C^1in x, by considering $h \gtrless 0$ separately, it follows that

$$|h_\infty(t)| \equiv |\lambda(x,t) - (x',t)| \leq K'|x-x'| \text{ for all } x,x' \text{ in } \overline{B}.$$

Likewise by writing

$$\lambda_n(x,t) = \lambda_o(x,0) + \int_0^t g(x,z,\theta_{n-1}(x,z),\lambda_n(x,z))\,dz,$$

it follows that

$$|\lambda_n(x,t) - \lambda_n(x,t')| \leq \left|\int_t^{t'} |g(x,z,\theta_{n-1}(x,z),\lambda_n(x,z))|\,dz\right|.$$

Since (θ_n) and (λ_n) are uniformly bounded for all n, it follows that

$$|\lambda(x,t) - \lambda(x,t')| \leq K|t - t'| \text{ for all } t,t' \leq T.$$

So it can be concluded that λ is of class C^1 in $\overline{D}_T$.

Thus, under the assumptions of the theorem θ and λ are certainly Holder continuous with exponent α in $\overline{D}_T$. This is sufficient to ensure that the system

$$L(\theta') = f(x,t,\theta,\lambda),$$

$$\frac{\partial\lambda'}{\partial t} = g(x,t,\theta,\lambda),$$

$$\theta' = \theta_o \text{ on } S_T \text{ and on } \overline{B} \text{ at } t = 0,$$

$$\lambda' = \lambda_o \text{ on } \overline{B} \text{ at } t = 0,$$

has a solution θ', λ' with θ' of class $C^{1+\beta}$ for any $0 < \beta < 1$ in D_T and also of class $C^{2+\gamma}$ for some $\gamma > 0$ in $\overline{D}_T$.

Now

$$L(\theta' - \theta_n) = \phi(x,t) \equiv f(x,t,\theta,\lambda) - f(x,t,\theta_n,\lambda_n),$$

and $\theta' - \theta_n = 0$ on the boundaries of D_T while, from Friedman's estimates (Theorem 3)

$$|\theta' - \theta_n| \leq P'|\phi(x,t)|.$$

But $\quad |\phi(x,t)| \leq M(|\theta - \theta_n| + |\lambda_n - \lambda|),$

and so as n tends to infinity through the values n_k the righthand side tends to zero. Hence θ' coincides with θ in $\overline{D}_T$ and so θ is of class $C^{1+\beta}$ in D_T and of class $C^{2+\gamma}$ in $\overline{D}_T$.

A similar argument using the equation

$$\frac{\partial\lambda'}{\partial t} = g(x,t,\theta,\lambda)$$

shows that λ' and λ coincide in $\overline{D}_T$. Thus $\partial\lambda/\partial t$ exists and moreover is of class C^1 in $\overline{D}_T$ since g, θ, and λ are also.

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