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TRANSIENT TEMPERATURE DISTRIBUTION
DURING AN EXOTHERMIC CHEMICAL REACTION

by

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Department of Mechanical Engineering

Prepared for the
Office of University Affairs
National Aeronautics and Space Administration

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The heat conduction equation for a material where heat is generated by a first order chemical reaction has been derived as a basic problem in heat conduction. Solutions have been obtained for a wall, sphere and cylinder when the influence of local temperature upon the heat generation rate may be suppressed. The validity of this restriction is determined in part by the magnitude of a dimensionless combination of material constants which has been designated as the reaction rate parameter v^2 . It has also been found that when a second parameter, $(E/RT_0^2)(H/\rho c)$, becomes small the appropriateness of the restriction increases independently of v^2 .

Introduction

There are several processes of technological interest in which a liquid-like material is poured into a mold and hardens as heat is liberated in the course of an exothermic chemical reaction. The resulting temperature distribution within the material may be potentially significant for at least one of two reasons. Within an inflammable material such as a solid propellant rocket grain, the peak temperature developed must not reach the ignition temperature of the propellant in order to avoid the problem of premature combustion. Secondly, the thermal stresses induced during solidification as a result of thermal gradients caused by the liberation of heat, may lead to residual stresses after hardening is completed which are detrimental to the integrity of the resulting structure. To solve either problem requires a complete knowledge of the temperature distribution during the hardening process.

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Introduction

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An examination of the available literature shows that the heat generation rate during an exothermic chemical reaction is related to the reaction rate considered in the theory of chemical kinetics, where the latter is exponentially dependent upon the local temperature. As a result, the partial differential heat conduction equation becomes non-linear and no exact analytical solutions are available^[1]. Existing results take the form of numerical solutions, or study the asymptotic behavior of the exact solution for special limiting cases. Thus Crank and Nicolson^[2] present a numerical solution by finite differences to the one dimensional problem of a wall of finite thickness, with convective boundary conditions, and heat generated within the wall by a first order chemical reaction. Similar results have been obtained by Nichols and Presson^[3] for the case of an infinitely long cylinder with prescribed surface temperature and heat liberated according to zeroth and first order chemical reactions. Anisimov and Perelman^[4] investigate the asymptotic behavior of the analytical solution for a wall with prescribed surface and initial temperature wherein heat is generated by initiating a zeroth order reaction. The results are obtained for large and small times, and for small values of the Pomarantsev or "explosion" parameter.

The literature search did not provide the authors with a temperature solution that would be amenable to their investigation of the thermal stresses induced during an exothermic chemical reaction which results in hardening of the reacting medium. Hence, the basic process was examined as a fundamental problem of heat transfer and an appropriate heat conduction equation containing a transient, temperature-dependent heat generation term was derived. The resulting partial differential equation was found to be of a form that is similar to those studied in the literature^[2,3,4]. Even though no exact analytic solution could be found for the derived non-linear heat conduction

[] Numbers in squared brackets refer to references listed in the bibliography

equation, it was observed that a solution can be extracted for restrictive conditions of temperature or heat generation. Specific solutions were obtained for a slab, a cylinder and a sphere under the required restrictive conditions. Not only are these solutions of use to the authors in their thermal stress studies, but they also add to the limited literature of the heat transfer problem.

The Heat Conduction Equation

The theory of the kinetics of chemical reactions shows that the rate at which a chemical reaction proceeds is determined by the character of the reaction. In a zeroth order chemical reaction, the reaction rate is independent of the concentration of the reactants which is fixed by the conditions of the reaction. Such a situation occurs, for example, under steady state conditions in a reacting bed, where material is supplied to the reaction externally in order to keep the concentrations constant. Thus, if W represents the concentration of some characteristic reactant, the rate at which this reactant is consumed is given by the equation^[5]

$$\frac{dW}{dt} = - C_1 e^{-E/RT} \quad (1)$$

where C_1 is the so-called pre-exponential factor, E is the activation energy, R is the universal gas constant and T the absolute temperature.

During a chemical reaction which occurs in a closed system, the reacting materials are consumed in the process. The relation between the rate at which the reaction proceeds then depends not only upon the temperature but also on the concentrations of the reactants. In the simplest case, the reaction rate is described by Equation (1) with W multiplying the right hand side^[5], and the result expressed as

$$\frac{dW}{dt} = -W C_1 e^{-E/RT} \quad (2)$$

This equation characterises a first order reaction. With N defined as the degree of reaction, the instantaneous concentration of reactants W is equal to $1-N$, a quantity which decreases from unity to zero as the reacting material is consumed. Equation (2) may then be written

$$\frac{dN}{dt} = (1-N) C_1 e^{-E/RT} \quad (3)$$

In an exothermic reaction, the rate of heat generation per unit volume may be assumed proportional to the rate at which the reactants are consumed. The reaction, when carried to completion, liberates a quantity of heat per unit volume which is designated H and called the volumetric heat of reaction. If $\dot{Q}(r',t)$ represents the instantaneous rate of heat generation with r' designated as the position vector, the quantity of heat liberated from the start of a reaction to a subsequent time t is given by the integral $\int_0^t \dot{Q}(r',t)dt$. Therefore, the degree of reaction N can also be measured by the expression $\frac{1}{H} \int_0^t \dot{Q}(r',t)dt$, and in view of Equation (3) the rate of heat generation can be written

$$\dot{Q}(r',t) = C e^{-E/RT} \left[1 - \frac{1}{H} \int_0^t \dot{Q}(r',t)dt \right] \quad (4)$$

where the constant C is equal to $H C_1$. Equation (4) couples the heat generation rate to the temperature distribution $T(r',t)$. Therefore, a complete solution of the problem requires the simultaneous consideration of the heat conduction equation.

In order to effect such a solution, it will be assumed for simplicity that thermal conductivity k , specific heat c , and density ρ remain constant

during the reaction. The thermal diffusivity $K = k/\rho c$ is then also constant. Under the foregoing conditions, the temperature distribution in a material subjected to a time varying internal heat generation is governed by the relation [1]

$$\nabla^2 T(r',t) + \frac{Q(r',t)}{k} = \frac{1}{K} \frac{\partial T}{\partial t} \quad (5)$$

The heat generation rate \dot{Q} may be eliminated between Equations (4) and (5). Rewriting (4) as

$$\frac{\dot{Q}}{1 - \frac{1}{H} \int_0^t \dot{Q} dt'} = C e^{-E/RT} \quad (6)$$

it follows that

$$-H \frac{\partial}{\partial t} \left[\ln \left\{ 1 - \frac{1}{H} \int_0^t \dot{Q} dt' \right\} \right] = C e^{-E/RT} \quad (7)$$

as may be seen by taking the indicated derivative. Integration of the preceding equation from time $t = 0$ to an arbitrary time t then gives

$$\ln \left\{ 1 - \frac{1}{H} \int_0^t \dot{Q} dt' \right\} = -\frac{C}{H} \int_0^t e^{-E/RT} dt' \quad (8)$$

Thus, forming exponentials of both sides of Equation (8) and introducing the result into Equation (4) permits the heat generation rate to be expressed as a function of temperature in the form

$$\dot{Q}(r',t) = C e^{-\frac{E}{RT} - \frac{C}{H} \int_0^t e^{-\frac{E}{RT}} dt'} \quad (9)$$

When $\dot{Q}(r',t)$ is replaced in Equation (5) by the preceding result, the transient heat conduction equation becomes

$$\nabla^2 T - \frac{1}{\kappa} \frac{\partial T}{\partial t} = - \frac{c}{k} e^{-\frac{E}{RT} - \frac{c}{H} \int_0^t e^{-\frac{E}{RT}} dt'} \quad (10)$$

The solution to the last equation, subject to suitable boundary and initial conditions provides the temperature distribution within a material undergoing a first order chemical reaction.

In order to simplify and generalize subsequent calculations, it is desirable to put Equation (10) into dimensionless form. For this purpose, let us define the dimensionless lengths

$$x = x'/L \quad ; \quad r = r'/R_0 \quad (11a)$$

where L and R_0 are some characteristic dimensions of the system, such as wall thickness and external radius respectively; the dimensionless time

$$\tau = \kappa t / L^2 \quad (11b)$$

the dimensionless temperature

$$\theta = RT/E \quad (11c)$$

the Pomarantsev or "explosion" parameter

$$P = CR_0^2 / \kappa E \quad (11d)$$

and the dimensionless group

$$\gamma = CL^2 / \kappa H \quad (11e)$$

With the preceding definitions, Equation (10) may be rewritten in dimensionless form as

$$\nabla^2 \theta - \frac{\partial \theta}{\partial \tau} = - Pe^{-1/\theta} e^{-\gamma \int_0^\tau e^{-1/\theta} d\tau'} \quad (12)$$

where ∇^2 now denotes the Laplacian operator written with respect to the dimensionless space coordinates.

The Pomarantsev parameter P plays a crucial role [4,6] in a zeroth order reaction. A steady state solution to the transient conduction equation does not exist if it exceeds a critical value. Instead, the temperature increases without limit during an exothermic reaction and an explosion will result. In a first order reaction, however, the temperature rise is limited by the available quantity of reactants and cannot exceed the amount $H/\rho c$. Unless this temperature rise triggers a secondary reaction, no explosion in the first sense is possible.

As cited in the Introduction, some numerical results to Equation (12) exist in the literature, but analytical solutions are not known to exist. Specific approximate analytical solutions will be derived in the present paper for the situation in which the initial temperature of a region as well as its surface temperature are constant and equal to T_0 . In dimensionless terms, the initial and boundary values of the temperature parameter θ will be designated θ_0 .

It is proposed that a solution for θ be generated in the following manner. Replace the term θ on the right side of Equation (12) with the constant θ_0 , so that the dimensionless temperature relation may be written

$$\nabla^2 \theta - \frac{\partial \theta}{\partial \tau} = - Pe^{-1/\theta_0} e^{-\gamma e^{-1/\theta_0} \tau} \quad (13)$$

Then define the reaction rate parameter

$$v^2 = \gamma e^{-1/\theta_0} \quad (14)$$

so that Equation (13) can be expressed

$$\nabla^2 \theta - \frac{\partial \theta}{\partial \tau} = - \frac{P}{\gamma} v^2 e^{-v^2 \tau} \quad (15)$$

It is now possible to solve Equation (15) directly for θ , and the solution designated $\theta_1(r, \tau)$, is the first approximation to the correct temperature distribution. A second approximation can be generated by substituting θ_1 into the right hand side of Equation (12), and solving the resulting non-homogeneous differential equation for that which is designated $\theta_2(r, \tau)$. By repeating the process, an iteration scheme is set up which hopefully will converge to the correct solution. Unfortunately, details become complicated and although the first approximation is readily obtained, integration required for the second approximation has proven to be unmanageable. Fortunately, however, the first approximation is of considerable interest under at least three physical conditions.

When all other quantities are kept constant, and the reaction rate parameter v^2 is sufficiently small, the resulting rise in the temperature will also be small. The variation of the exponential factor $\exp(-E/RT)$ is then small, and Equation (11) may be represented by Equation (15).

At the other extreme, we have a very large reaction rate parameter. The material then hardens quickly and the heat is liberated impulsively. The material undergoes an instantaneous and uniform rise in temperature equal to $H/\rho c$, followed by a cooling rate that is independent of the reaction rate parameter as well as the temperature. The solutions of Equation (15) then approach the exact solution of Equation (11).

It should be pointed out in view of Equations (11c), (11e) and (14) that the definition of the reaction rate parameter may also be written

$$v^2 = \frac{CL^2}{KH} e^{-E/RT_0} \quad (16)$$

and thus involves quantities other than those which govern the physical speed of the reaction. Large and small values of v^2 associated with rapid and slow hardening must, therefore, be identified with the time scale of the Fourier number $(\kappa t/L^2)$, and not with physical time.

The maximum temperature change which will result from an impulsive liberation of heat is equal to $H/\rho c$. If during that temperature change from T_0 to $T_0 + H/\rho c$ there is only a small change in the exponential factor $e^{-E/RT}$, then in an approximate sense, the heat generation rate becomes independent of the temperature. The solutions of Equation (15) will thus approach those of Equation (11) independently of the value of the reaction rate parameter.

Except for circumstances cited, the results obtained from Equation (15) are expected to be qualitatively similar but quantitatively different from the solutions of Equation (11).

Equation (15) may also be written

$$\nabla^2 \theta - \frac{\partial \theta}{\partial \tau} = -\beta e^{-v^2 \tau} \quad (17)$$

by defining the coefficient Pv^2/γ to be equal to the parameter β . The latter form will prove to be useful in subsequent analysis.

Let us now direct our remarks to the boundary condition and initial conditions of the problem. During an actual casting process the mold wall, and the surfaces between the mold, cast material, and the ambient fluid form a thermal barrier to heat flow. The usual mathematical description of

this effect takes the form of a convective boundary condition. However, when the mold is physically thin, and the material highly conductive, the accumulated thermal resistance can be negligible. Furthermore, during the curing process, the mold surface may be cooled and kept at a fixed temperature in order to maintain temperature control. Under the foregoing conditions, the ambient temperature may be considered the same as the surface temperature of the poured material. The latter situation suggests the boundary and initial conditions for the present study. It will therefore be assumed in solving Equation (17) that for the

$$\text{Boundary condition: } \theta_{\text{surface}} = \theta_0 \quad (18a)$$

and for the

$$\text{Initial condition: } \theta(r,0) = \theta_0 \quad (18b)$$

Temperature Solution for an Infinite Slab

Let us consider the problem of casting an infinite slab of constant thickness L . The initial temperature of the cast material is T_0 and the surfaces of the mold are maintained at T_0 . The resulting temperature variation is a function of only one space coordinate, that which is measured normal to the mold surface; in dimensionless form it is given the range $0 \leq x \leq 1$. Consequently, the Laplacian operator reduces to the second derivative with respect to x , and Equation (17) for the dimensionless temperature parameter θ , becomes

$$\frac{\partial^2 \theta}{\partial x^2} - \frac{\partial \theta}{\partial \tau} = -\beta e^{-\nu^2 \tau} \quad (19)$$

The associated boundary and initial conditions may be simplified to read

$$\text{Boundary conditions: } \theta(x, \tau) = 0 ; x = 0, x = 1 \quad (20a)$$

$$\text{Initial condition: } \theta(x, 0) = 0 \quad (20b)$$

because Equation (19) determines θ to within a constant, and θ can be measured with respect to θ_0 .

To find the complete solution to Equation (19) note that its homogeneous solution may be found by separation of variables to read

$$\theta_H = \sum_n^{\infty} e^{-\lambda_n^2 \tau} [A_n \sin \lambda_n x + B_n \cos \lambda_n x] , \quad (21)$$

$$n = 1, 2, 3, \dots$$

The particular solution is assumed to be of the form $\theta_p = e^{-v^2 \tau} \phi(x)$.

When substituted into Equation (19), it is found that

$$\phi(x) = A_p \sin vx + B_p \cos vx - \frac{\beta}{v^2} \quad (22)$$

and consequently the complete solution takes the form

$$\begin{aligned} \theta(x, \tau) = & e^{-v^2 \tau} \left[A_p \sin vx + B_p \cos vx - \frac{\beta}{v^2} \right] \\ & + \sum_n^{\infty} e^{-\lambda_n^2 \tau} [A_n \sin \lambda_n x + B_n \cos \lambda_n x] , \end{aligned} \quad (23)$$

$$n = 1, 2, 3, \dots$$

The boundary conditions at $x = 0$ and $x = 1$ are satisfied if

$$A_p = -\frac{\beta}{v^2} [\cot v - \csc v] ; B_p = \frac{\beta}{v^2} \quad (24)$$

$$\lambda_n = n\pi, n = 1, 2, 3 \dots ; B_n = 0$$

The solution at this point, therefore, can be written

$$\theta(x,\tau) = \frac{\beta}{v^2} e^{-v^2\tau} [(\csc v - \cot v) \sin vx + \cos vx - 1] + \sum_n^{\infty} A_n e^{-(n\pi)^2\tau} \sin n\pi x ; \quad n = 1,2,3 \dots \quad (25)$$

The initial condition requires that

$$\theta(x,0) = 0 = \frac{\beta}{v^2} [(\csc v - \cot v) \sin vx + \cos vx - 1] + \sum_n^{\infty} A_n \sin n\pi x , \quad n = 1,2,3 \dots \quad (26)$$

or

$$-\frac{\beta}{v^2} [(\csc v - \cot v) \sin vx + \cos vx - 1] = \sum_n^{\infty} A_n \sin n\pi x , \quad n = 1,2,3 \dots \quad (27)$$

When the left side of Equation (27) is expressed in a Fourier series^[7] consisting of terms in $\sin n\pi x$, the coefficients A_n are found to be equal to

$$A_n = \frac{4\beta}{n\pi[v^2 - (n\pi)^2]} , \quad n = 1,3,5, \dots \quad (28)$$

Therefore the solution to Equation (19) with the prescribed boundary and initial conditions of Equation (20) may be written

$$\theta(x,\tau) = \frac{\beta e^{-v^2\tau}}{v^2} [(\csc v - \cot v) \sin vx + \cos vx - 1] + 4\beta \sum_n^{\infty} \frac{e^{-(n\pi)^2\tau} \sin n\pi x}{n\pi[v^2 - (n\pi)^2]} ; \quad n = 1,3,5, \dots \quad (29)$$

The preceding result can be put into a more compact form by noting that at $\tau = 0$

$$\theta(x,0) = 0 = \frac{\beta}{v^2} \left[(\csc v - \cot v) \sin vx + \cos vx - 1 \right] \quad (30)$$

$$+ 4\beta \sum_n^{\infty} \frac{\sin n\pi x}{n \pi [v^2 - (n\pi)^2]}, \quad n = 1, 3, 5 \dots$$

or therefore

$$(\csc v - \cot v) \sin vx + \cos vx - 1 = 4v^2 \sum_n^{\infty} \frac{\sin n\pi x}{n \pi [(n\pi)^2 - v^2]} \quad (31)$$

$$n = 1, 3, 5 \dots$$

When Equation (31) is substituted into Equation (29) and both series placed under one summation sign, it is found that the temperature distribution within a slab in which the material is generating heat at an exponentially decaying rate is given by the relatively simple expression

$$\theta(x,\tau) = 4\beta \sum_n^{\infty} \frac{(e^{-v^2\tau} - e^{-(n\pi)^2\tau})}{n \pi [(n\pi)^2 - v^2]} \sin n\pi x ; \quad (32)$$

$$n = 1, 3, 5, \dots$$

The significance of this expression will be discussed after an equivalent examination of the temperature distribution in a sphere and in an infinitely long cylinder.

Temperature Solution for a Solid Sphere

Under conditions of spherical symmetry, the Laplacian operator reduces to a function of the radial derivatives, and consequently Equation (17) for the dimensionless temperature distribution within a material generating heat according to a first order chemical reaction can be written

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \theta}{\partial r} \right) - \frac{\partial \theta}{\partial \tau} = -\beta e^{-v^2\tau} \quad (33)$$

The dimensionless coordinate r is equal to r'/R_0 where r' is the dimensional radial coordinate, and R_0 the outer radius of the sphere. For the same physical reasons presented in the previous section, the boundary and initial conditions associated with Equation (33) may be written

$$\theta(1,\tau) = 0 \quad (a) \quad , \quad \theta(r,0) = 0 \quad (b) \quad (34)$$

In addition, of course, there exists the assertion that the solution be nonsingular at the origin. With $V = r\theta$, Equation (33) reduces to

$$\frac{\partial^2 V}{\partial r^2} - \frac{\partial V}{\partial \tau} = -\beta r e^{-v^2 \tau} \quad (35)$$

The homogeneous solution to Equation (35) is found by separation of variables to be

$$V_H = \sum_n^{\infty} e^{-\lambda_n^2 \tau} [A_n \sin \lambda_n r + B_n \cos \lambda_n r] \quad , \quad n = 1, 2, 3 \dots \quad (36)$$

whereas the particular solution may be written

$$V_p = e^{-v^2 \tau} [A_p \sin vr + B_p \cos vr - \frac{\beta r}{v^2}] \quad (37)$$

The complete solution is equal to the sum of V_p and V_H . When V is replaced by $r\theta$, the complete solution for the dimensionless temperature distribution takes the form

$$\begin{aligned} \theta(r,\tau) = & \frac{e^{-v^2 \tau}}{r} [A_p \sin vr + B_p \cos vr - \frac{\beta r}{v^2}] \\ & + \sum_n^{\infty} \frac{e^{-\lambda_n^2 \tau}}{r} [A_n \sin \lambda_n r + B_n \cos \lambda_n r] \quad , \end{aligned} \quad (38)$$

$$n = 1, 2, 3, \dots$$

At the origin the terms containing $\cos(vr)$ and $\cos(\lambda_n r)$ become infinite but are eliminated from the solution by causing B_p and B_n to vanish. Boundary condition (34a) requires θ to vanish at the outer radius, a requirement that is satisfied when $A_p = \beta/v^2 \sin v$ and $\lambda_n = n\pi$, $n = 1, 2, 3, \dots$. Thus Equation (38) can be written

$$\theta(r, \tau) = \frac{e^{-v^2 \tau}}{r} \left[\frac{\sin vr}{\sin v} - r \right] \cdot \frac{\beta}{v^2} + \sum_n^{\infty} \frac{e^{-(n\pi)^2 \tau}}{r} A_n \sin n\pi r, \quad (39)$$

$$n = 1, 2, 3, \dots$$

Initial condition (34b) requires that

$$\theta(r, 0) = 0 = \frac{\beta}{v^2} \left[\frac{\sin vr}{\sin v} - r \right] + \sum_n^{\infty} A_n \sin n\pi r, \quad n = 1, 2, 3, \dots \quad (40)$$

or

$$\frac{\beta}{v^2} \left[r - \frac{\sin vr}{\sin v} \right] = \sum_n^{\infty} A_n \sin n\pi r, \quad n = 1, 2, 3, \dots \quad (41)$$

The Fourier coefficients A_n are determined to be

$$A_n = \frac{2\beta(-1)^n}{n\pi[(n\pi)^2 - v^2]}, \quad n = 1, 2, 3, \dots \quad (42)$$

and consequently, the solution of Equation (33), subject to the given boundary and initial conditions, can be expressed

$$\theta(r, \tau) = \frac{\beta}{v^2} \cdot \frac{e^{-v^2 \tau}}{r} \left[\frac{\sin vr}{\sin v} - r \right] + \sum_n^{\infty} \frac{2\beta(-1)^n}{n\pi[(n\pi)^2 - v^2]} \frac{e^{-(n\pi)^2 \tau}}{r} \sin n\pi r \quad (43)$$

$$n = 1, 2, 3, \dots$$

It is seen, as a consequence of Equation (41) and Equation (42) that at $\tau = 0$, the series given by the second term represents the negative of

the radially dependent coefficient

$$\frac{\beta}{v^2 r} \left[\frac{\sin vr}{\sin v} - r \right] = - \sum_n \frac{2\beta(-1)^n}{n(n\pi)^2 - v^2} \cdot \frac{\sin n\pi r}{n\pi r}, \quad n = 1, 2, 3, \dots \quad (44)$$

Thus Equation (43) can be written more compactly as

$$\theta(r, \tau) = 2\beta \sum_n \frac{(-1)^n}{n} \frac{e^{-(n\pi)^2 \tau} - e^{-v^2 \tau}}{(n\pi)^2 - v^2} \frac{\sin n\pi r}{n\pi r}; \quad (45)$$

$n = 1, 2, 3, \dots$

Equation (45) approximates the temperature distribution within a sphere with a time-dependent generation of heat due to first order chemical reaction.

Solution for an Infinitely Long Cylinder

In cylindrical coordinates with axial symmetry, Equation (17) reduces to

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta}{\partial r} \right) - \frac{\partial \theta}{\partial \tau} = - \beta e^{-v^2 \tau} \quad (46)$$

The dimensionless coordinate r is equal to r'/R_0 where r' is the dimensional radial coordinate, and R_0 is the outer radius of the cylinder. For reasons previously indicated, the boundary and initial conditions for the problem may be expressed

$$\theta(1, \tau) = 0 \quad (a) \quad ; \quad \theta(r, 0) = 0 \quad (b) \quad (47)$$

with the understanding that the solution be non-singular at the center. Separation of variables shows the homogeneous solution of Equation (46) to be

$$\theta_H = \sum_n e^{-\lambda_n^2 \tau} [A_n J_0(\lambda_n r) + B_n Y_0(\lambda_n r)] , \quad (48)$$

$$n = 1, 2, 3, \dots$$

in which J_0 is the zeroth order Bessel function of the first kind, and Y_0 is the zeroth order Bessel function of the second kind. With a particular solution of the form $\theta_p = e^{-v^2 \tau} \phi(r)$, Equation (46) shows that ϕ satisfies the relation

$$r^2 \frac{d^2 \phi}{dr^2} + r \frac{d\phi}{dr} + \left(\frac{\beta}{v^2} + \phi \right) v^2 r^2 = 0 \quad (49)$$

The latter is a Bessel equation of zeroth order. Its solution is

$$\phi(r) = A_p J_0(vr) + B_p Y_0(vr) - \frac{\beta}{v^2} \quad (50)$$

where A_p and B_p are constants. Hence the complete solution to Equation (46) may be written

$$\theta(r, \tau) = e^{-v^2 \tau} \left[A_p J_0(vr) + B_p Y_0(vr) - \frac{\beta}{v^2} \right] \quad (51)$$

$$+ \sum_n e^{-\lambda_n^2 \tau} [A_n J_0(\lambda_n r) + B_n Y_0(\lambda_n r)] , \quad n = 1, 2, 3, \dots$$

Since the Bessel function $Y_0(\lambda r)$ becomes infinitely large at $r = 0$, the constants B_p and B_n must vanish identically for the preceding solution to be finite at the origin. At the outer radius of the cylinder, the boundary condition requires that $\theta(1, \tau) = 0$. This condition is satisfied when $A_p = \beta/v^2 J_0(v)$ and λ_n are roots of $J_0(\lambda_n) = 0$. Substitution of the preceding conclusions into Equation (51) allows it to be written

$$\theta(r, \tau) = \frac{\beta}{v^2} e^{-v^2 \tau} \left[\frac{J_0(vr)}{J_0(v)} - 1 \right] + \sum_n A_n e^{-\lambda_n^2 \tau} J_0(\lambda_n r) , \quad (52)$$

$n = 1, 2, 3, \dots$

The initial condition on θ , prescribed by Equation (47b) indicates that

$$\theta(r, 0) = 0 = \frac{\beta}{v^2} \left[\frac{J_0(vr)}{J_0(v)} - 1 \right] + \sum_n A_n J_0(\lambda_n r) , \quad (53)$$

$n = 1, 2, 3, \dots$

or therefore

$$-\frac{\beta}{v^2} \left[\frac{J_0(vr)}{J_0(v)} - 1 \right] = \sum_n A_n J_0(\lambda_n r) , \quad n = 1, 2, 3, \dots \quad (54)$$

The coefficients A_n may be determined by developing the left side of Equation (54) into a Fourier-Bessel series^[8]. It is then found that

$$A_n = \frac{\frac{\beta}{v^2} \int_0^1 r \left[1 - \frac{J_0(vr)}{J_0(v)} \right] J_0(\lambda_n r) dr}{J_1^2(\lambda_n)/2} \quad (55)$$

Evaluation of the integral shows that

$$A_n = \frac{2\beta}{\lambda_n [v^2 - \lambda_n^2] J_1(\lambda_n)} \quad (56)$$

Thus the solution to Equation (46) under the prescribed boundary and initial conditions of Equation (47) can be written

$$\theta(r, \tau) = \frac{\beta}{v^2} e^{-v^2 \tau} \left[\frac{J_0(vr)}{J_0(v)} - 1 \right] - 2\beta \sum_n \frac{e^{-\lambda_n^2 \tau} J_0(\lambda_n r)}{\lambda_n [\lambda_n^2 - v^2] J_1(\lambda_n)} , \quad (57)$$

$n = 1, 2, 3, \dots$

The previous expression can be simplified by noting that at $\tau = 0$

$$\theta(r,0) = 0 = \frac{\beta}{v^2} \left[\frac{J_0(vr)}{J_0(v)} - 1 \right] - 2\beta \sum_n \frac{J_0(\lambda_n r)}{\lambda_n [\lambda_n^2 - v^2] J_1(\lambda_n)}, \quad (53)$$

$$n = 1, 2, 3, \dots$$

so that

$$\frac{\beta}{v^2} \left[\frac{J_0(vr)}{J_0(v)} - 1 \right] = 2\beta \sum_n \frac{J_0(\lambda_n r)}{\lambda_n [\lambda_n^2 - v^2] J_1(\lambda_n)}, \quad (59)$$

$$n = 1, 2, 3, \dots$$

Substitution of Equation (59) into Equation (57) followed by a combination of the two series under one summation sign yields the temperature distribution in an infinitely long cylinder, where the material generates heat due to a first order chemical reaction, in the form

$$\theta(r,\tau) = 2\beta \sum_n \frac{e^{-v^2\tau} - e^{-\lambda_n^2\tau}}{\lambda_n [\lambda_n^2 - v^2]} \cdot \frac{J_0(\lambda_n r)}{J_1(\lambda_n)}; \quad n = 1, 2, 3, \dots \quad (60)$$

Determination of Coefficients

To make a quantitative examination of the temperature distribution associated with the solutions given in Equations (32), (45) and (60), it is necessary to assign suitable numerical values to the constants contained therein. Precise values can be assigned in a specific investigation. In the present situation, a more general point of view may be taken before making the assignment, by first exploring the significance of the expression previously defined as the degree of reaction N .

The quantity $N(t)$ which specifies the extent to which the chemical reaction has gone to completion, may be expressed in terms of the heat generation rate and the heat of reaction as

$$N(r,t) = \frac{1}{H} \int_0^t \dot{Q}(r',t') dt' \quad (61)$$

In view of Equation (6), the integral containing the heat generation rate can be eliminated, leaving

$$N(r,t) = 1 - \frac{\dot{Q}(r,t)}{C e^{-E/RT}} \quad (62)$$

Since the heat generation rate is itself expressible solely in terms of the temperature, it may be replaced in the preceding equation by its equivalent in terms of temperature from Equation (9), so that

$$N(r,t) = 1 - e^{-\frac{C}{H} \int_0^t e^{-E/RT} dt'} \quad (63)$$

If the temperature T does not vary appreciably from its initial value T_0 (as assumed in each of the three solutions for temperature distribution, derived earlier in this report), or if the heat generation rate is not appreciably influenced by the temperature changes induced in the material, Equation (63) reduces to

$$N(t) = 1 - e^{-\frac{C}{H} \cdot e^{-1/\theta_0} t} \quad (64)$$

where, in accordance with Equation (11c) E/RT_0 has been replaced by its equivalent θ_0 . Then, in view of the definition of v^2 given by Equation (16) and τ given by Equation (11b), the degree of reaction is expressible in the simple form

$$N(\tau) = 1 - e^{-v^2\tau} \quad (65)$$

One may use the last expression to determine a physically valid range of values for the parameter v^2 based upon observation of hardening times and thermal diffusivity. Although mathematically it takes an infinite τ for the reaction to reach completion and N to take on the value 1, one can observe that the limiting value is reached asymptotically. For all practical purposes it is reasonable to assume that the reaction has been completed when N takes on some value close to unity, let us say arbitrarily 0.9. The numerical value of $v^2\tau$ is then about 2.30. It is further noted in our reasoning that the physical time required to fabricate or cure materials where setting occurs by chemical reaction, may range anywhere from 1 to 100 hours. Also, the characteristic length or radius of the physical configurations under examination may run from 0.1 foot to 10 feet. With dimensionless time given as $\tau = \kappa t'/L^2$, where t' is the setting time, and $v^2\tau = 2.3$ according to the preceding assumption, the parameter $v^2 = 2.3/(\kappa t'/L^2)$. Let us take the thermal diffusivity κ to be .004 ft²/hr, a numerical value found for many plastic materials. It is then seen that v^2 has a range of values from about 0.5 to 500, (the small value was obtained by using the assumed numerical values of a large setting time and small size, while the larger value was obtained for a short setting time and a large size).

The parameter β which first appears in Equation (17) and then is found throughout the analysis, can be expressed with the aid of Equations (11d) and (11e) in terms of v^2 by the relation

$$\beta = v^2 \cdot R/E \cdot H/\rho c \quad (66)$$

Since the dimensionless temperature θ is equal to RT/E , substitution

for β and θ into Equations (32), (45) and (60) puts them into a form which expresses the dimensional temperature. Thus for the wall

$$T(x, \tau) = 4v^2 \cdot \frac{H}{\rho c} \sum_n \frac{(e^{-v^2 \tau} - e^{-(n\pi)^2 \tau})}{n\pi[(n\pi)^2 - v^2]} \sin n\pi x, \quad (67)$$

$n = 1, 3, 5, \dots$

For the sphere

$$T(r, \tau) = 2v^2 \cdot \frac{H}{\rho c} \sum_n (-1)^n \frac{(e^{-(n\pi)^2 \tau} - e^{-v^2 \tau})}{\Gamma[(n\pi)^2 - v^2]} \frac{\sin n\pi r}{n\pi r}, \quad (68)$$

$n = 1, 2, 3, \dots$

For the cylinder

$$T(r, \tau) = 2v^2 \cdot \frac{H}{\rho c} \sum_n \frac{(e^{-v^2 \tau} - e^{-\lambda_n^2 \tau})}{\lambda_n[\lambda_n^2 - v^2]} \cdot \frac{J_0(\lambda_n r)}{J_1(\lambda_n)}, \quad (69)$$

$n = 1, 2, 3, \dots$

The ratio $H/\rho c$ is dimensionally a temperature, and measures the increase in temperature which would occur if the heat of reaction per unit volume H were to be discharged into the material instantaneously. It corresponds to the temperature after the initial instant in the limit as v^2 becomes very large, and is also the maximum possible temperature increase under any circumstances for the first order reaction.

Numerical Results and Discussion

Equations have been presented which express the temperature distribution within a wall, sphere, and cylinder where heat is generated by a first order chemical reaction when the temperature does not vary appreciably from its initial value or if the heat generation rate is not appreciably

influenced by the temperature change induced in the material. In order to obtain some idea of the significance of either one of the restrictions, please note that the temperature effect is due to the factor $\exp(-E/RT)$ which appears first in Equation (1). For many organic resins, the activation energy E has a range of from 20,000 to 40,000 BTU/lb - mole^[3]. If the reaction is initiated at 70°F, it is easily determined that a rise in the temperature of 18° in the first instance to 9° in the second is sufficient to cause the factor $\exp(-E/RT)$ to double. Under these circumstances, the reaction rate is strongly influenced by temperature, and the sensitivity increases with the magnitude of the activation energy. Thus, for low values of v^2 , the approximate solutions will be valid only if the temperature rise is indeed small, or when the reactions have a low activation energy. It can also be seen from Equation (16) that for a suitable combination of physical constants, v^2 may become large. As we have just seen, temperature has the effect of accelerating the reaction and thus increasing the effective value of v^2 . It has already been observed, however, that for very large values of v^2 the temperature distribution over most of time is independent of the temperature, since the generation of heat has ceased. Thus the approximate solutions will also be valid for these large values of v^2 .

Since the temperature exerts its influence upon the heat generation rate through the presence of the factor $\exp(-E/RT)$, it is the variation of this factor which, to a great extent determines the accuracy of the present solutions. The maximum temperature rise under any circumstances is limited to $H/\rho c$, so that the ratio of the exponential factors under the extreme limits of the initial and maximum temperature can be written

$$\frac{e^{-\frac{E}{RT_0 + R(H/\rho c)}}}{e^{-\frac{E}{RT_0}}} = e^{\frac{E}{RT_0} \left[\frac{H/\rho c}{T_0 + H/\rho c} \right]} \quad (70)$$

The variation of the exponential factor decreases as the foregoing approaches unity, and this condition will be met, approximately, whenever the dimensionless group $E/RT_0^2 \cdot H/\rho c$ is very small. Thus, independently of the parameter v^2 or the rate of reaction, the more closely the preceding condition is satisfied, the more appropriate will be the solutions presented in the present paper.

The numerical results which are obtained for the three geometrical configurations studied are qualitatively similar, and it suffices for illustrative purposes here to exhibit graphs and tables for one of these, the infinitely long cylinder. Figure 1 shows the temperature history at the center of the cylinder for several values of the parameter v^2 . Values of the temperature are plotted as a fraction of the maximum attainable temperature increase $H/\rho c$. For a value of v^2 equal to unity, the maximum temperature rise in the cylinder reaches 0.18 of the maximum attainable temperature rise. In view of the preceding discussion, and depending upon the activation energy, this can be sufficiently large to influence the heat generation rate. At the other extreme, we note that when v^2 equals or exceeds 100, the maximum temperature is greater than .90 of the attainable maximum increase, and the subsequent cooling follows the same path as for v^2 equal to 500 and presumably larger values. Thus, in this range of values for v^2 , the solution will, along the centerline, approximate the actual temperature history resulting from the reaction quite well. From Equation (16) we observe that v^2 is a function of the dimensions and thermal properties of the system as well as of the reaction constants. Thus, a given

physical reaction rate can, in different contexts, lead to large or small values of v^2 .

Figure 2 shows the dimensionless temperature distribution within the cylinder at the moment at which the center reaches the maximum temperature. The distribution, which has been normalised so that the magnitude at the center is unity, is shown for differing values of v^2 . With increasing values of v^2 , it is evident that there is an ever larger central region of almost constant temperature at this instant. In the limit when v^2 becomes very large and the heat is liberated impulsively throughout the material, the temperature ratio at the time of the centerline maximum is of course unity throughout. It thus appears that the closeness of the approximation with increasing values of v^2 varies spatially as well as in time. For a given value of v^2 , the center temperature as determined by the solution presented here may reproduce the actual temperature during the reaction closely, whereas points nearer to the surface may still be considerably in error, thus indicating that convergence of the linearized solution to the exact solution is not necessarily uniform spatially.

Some qualitative inferences may also be drawn from the results indicated in Table 1. One may be inclined intuitively to judge the degree of hardening in a thermosetting material from the temperature, assuming that if the material still exhibits an elevated temperature, the reaction is not yet completed. On the contrary, Table 1 shows that for large values of v^2 , corresponding to a rapid hardening, the material is completely hardened at the time that the centerline temperature attains its maximum value. On the other hand, when v^2 is small, the major part of the reaction can occur well after the time of maximum temperature. Thus, one cannot judge the degree of reaction solely from temperature data.

Similar conclusions may be drawn from the results for the slab and sphere.

Conclusion

The problem of determining the temperature distribution in a material where heat is generated by a first order chemical reaction has been discussed, and the non-linear character of the resulting heat conduction equation exhibited. Suitable solutions for a wall, sphere, and cylinder were obtained by suppressing the effect of temperature upon the heat generation rate, and conditions under which this approximation would be valid were studied.

It was determined that the validity of the approximation depended in part upon a combination of constants designated as the reaction rate parameter v^2 , and that the approximation became quantitatively accurate when v^2 was either very large or very small. For small values of v^2 , the closeness of the approximation also depended upon the temperature rise and the activation energy. At intermediate values of v^2 , the approximate solution was qualitatively similar to the expected form of the actual temperature distribution, but no quantitative inferences could be drawn.

It was observed that the sensitivity of the heat generation rate to temperature changes was determined by the magnitude of the activation energy. For chemical reactions with low activation energy, the influence of temperature upon the heat generation rate is small, and the solution presented here will yield quantitatively accurate results. This will occur when the variation of the factor $\exp(-E/RT)$ over the range of temperatures predicted by the approximate solution is small. If the activation energy is large, the approximate solution will be quantitatively accurate only for very large and very small values of the dimensionless reaction rate parameter v^2 . It has also

been shown that the influence of the temperature upon the heat generation rate decreases with the magnitude of the factor $(E/RT_0^2)(H/\rho c)$, and that as this factor becomes small, the accuracy of the approximation increases independently of the parameter v^2 .

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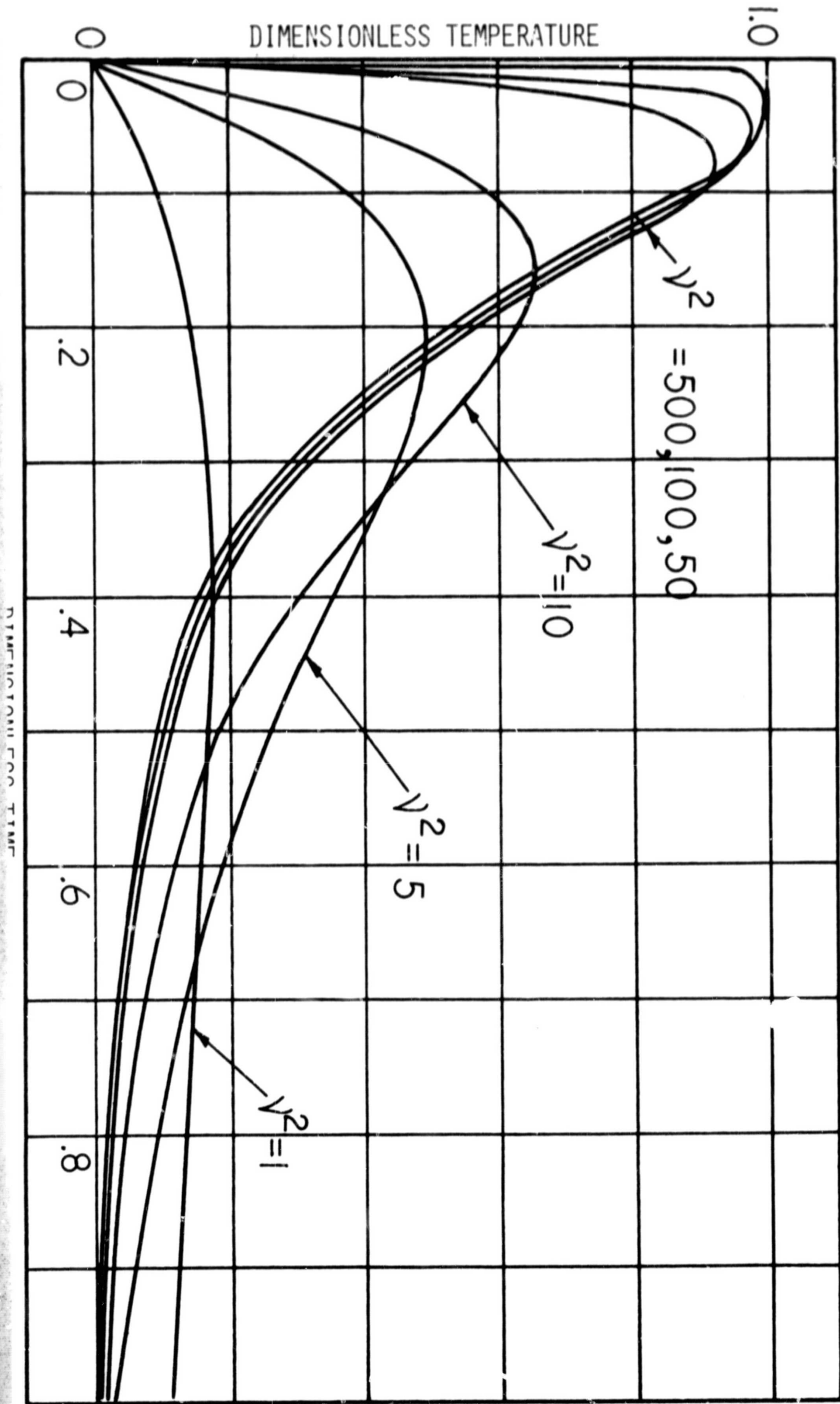


Figure 1 -
 Temperature History
 on the Centerline
 of an Infinitely
 Long Cylinder for
 Several Values of
 the Reaction Rate
 Parameter

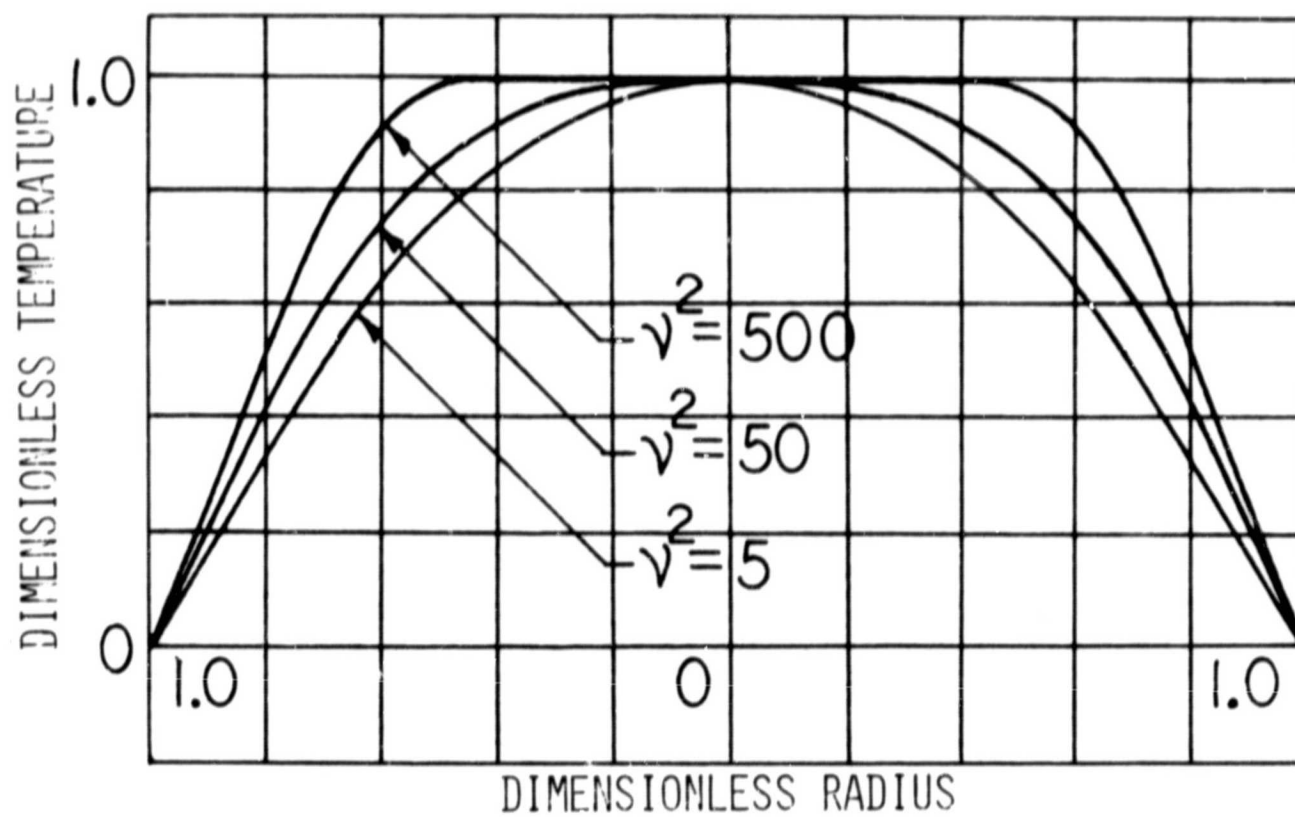


Figure 2 - Ratio of Local to Centerline Temperature
at Instant of Maximum Centerline Temperature
vs. Radial Position in the Cylinder
for Several Values of the
Reaction Rate Parameter

$\sqrt{2}$	DEGREE OF REACTION	DIMENSIONLESS TIME AT MAXIMUM TEMPERATURE	MAXIMUM TEMPERATURE ON CENTERLINE
.50	.22	.50	.10
1.00	.33	.40	.17
5.00	.63	.20	.48
10.00	.78	.15	.65
50.00	.97	.07	.95
100.00	.99	.05	.99
500.00	1.00	.03	1.00

Table 1 - Variation of the Degree of Reaction and Dimensionless Time with Reaction Rate at Time of Maximum Centerline Temperature in the Cylinder