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DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH AND FIRE OFFICES' COMMITTEE
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ON AN APPROXIMATION IN THE THEORY OF SELF-HEATING

by

P.H. Thomas

Summary

In transient self-heating problems the spatial variation in symmetrically heated bodies is often assumed to be uniform and an effective surface transfer coefficient is defined so that the analysis of self heating problems can be simplified. It is shown here how this approximation can be extended to allow for a known degree of surface cooling.

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Introduction

The thermal theory of explosion(1) is derived from considerations of the thermal balance of a material in which heat is lost by conduction to the surface and in which heat is generated by a temperature dependent reation. Because conduction heat loss varies linearly with temperature while the rate of reaction increases faster than linearly, equilibrium is only possible under certain conditions, and the problem is to find these. In this paper we shall consider an approximate method by means of which the problem can be reduced to the simple formulation originally given by Semenoff even with a boundary condition involving surface cooling.

We assume a zero order reaction obeying the Arrhenius Law and an isotropic material with thermal and chemical properties that are independent of temperature. The conventional differential equation for the conservation of heat between heat conduction, sensible heat and heat generation for the transient state may be written as

$$\frac{\partial^2 \theta}{\partial z^2} + \frac{k}{z}\frac{\partial \theta}{\partial z} = \frac{\partial \theta}{\partial \tau} - \delta_{\cdot} e^{\theta} \qquad \text{......(1)}$$

Most of the notation follows that used by other authors on this subject.

Thus $\theta = \frac{E(T-T_0)}{R\,T_0^2}$ a dimensionless temperature

$\delta = \frac{Q.f.E.r^2 e^{-\frac{E}{RT_0}}}{\lambda.R.T_0^2}$ a dimensionless reaction rate

$z = \frac{x}{r}$ a dimensionless distance

$\tau = \frac{a t}{r^2}$ a dimensionless time

and k is a number which is zero for the slab. 1 for the cylinder and 2 for the sphere

and E is the activation energy
R is the universal gas constant
T is the absolute temperature
Q is the heat of reaction
f is the pre-exponential constant
r is the half-width of the slab or the radius
λ is the thermal conductivity
a is the thermal diffusivity
and t is time.

We have the boundary conditions

$$\frac{\partial\theta}{\partial z} = 0 \quad \text{at} \quad z = 0 \qquad \text{......(2)}$$

$$\alpha\,\theta + \frac{\partial\theta}{\partial z} = 0 \quad \text{at} \quad z = \pm 1 \qquad \text{......(3)}$$

where $\alpha = \dfrac{Hr}{\lambda}$

and H is the surface cooling coefficient. If S & V are surface area and volume the expression sometimes used in the literature HS/V reduces here to $(1+k)H/r$.

Equation 1 is itself approximate in that the Arrhenius term is approximated by

$$e^{-\frac{E}{RT}} \doteq e^{-E/RT_0} \cdot e^{\theta}$$

This approximation has been widely used, in particular by Frank Kamenetski in his treatment of the critical parameter(2). Gray and Harper(3) have employed the quadratic approximation

$$e^{-\frac{E}{RT}} \doteq e^{-\frac{E}{RT_0}}\left(1 + 0.72\,\theta + \theta^2\right)$$

in the approximate form.

The equation for transient problems is greatly simplified if(4)(5)(6) $\frac{\partial^2\theta}{\partial z^2} + \frac{k}{z}\frac{\partial\theta}{\partial z}$ can be replaced by, say, $-(1+k)\beta_k\,\theta$ where β_k is some constant. Such a replacement gives the same equation as Semenoff's(1) original assumption that the temperature is uniform except that the constant β replaces the real transfer coeficient Hr/λ i.e. α. Using this form of equation 1 we find the critical values of δ given by

$$\delta_c = \frac{(1+k)\beta_c}{e} \qquad \text{......(4i)}$$

or

$$\frac{(1+k)\alpha}{e} \qquad \text{......(4ii)}$$

When δ is proportional to α and the critical condition is that δ/α is a constant we see from the definitions that the critical condition does not involve λ and only involves one power of τ. This is Semenoff's original formulation[1]. The substitution for $\frac{\partial^2 \theta}{\partial z^2} + \frac{k}{z}\frac{\partial \theta}{\partial z}$ by $-(1+k)\beta\theta$ does just the same if β is defined by some arbitrary heat transfer coefficient. Here β is not yet identified with any physical parameter but it is expected to be a function of α and approximately equal to α when $\alpha \rightarrow 0$. Frank Kamenetski [7] has in fact used equation 4 to obtain $\beta_{k,\infty}$ the particular values of β_k that gives the correct value of δ for $\alpha \rightarrow \infty$. The exact solution of equation 1 has been given[8] for an arbitrary value of α but it is desirable to obtain a more flexible approximate result. We show the relation between the various approaches in Fig.1 which is diagrammatic.

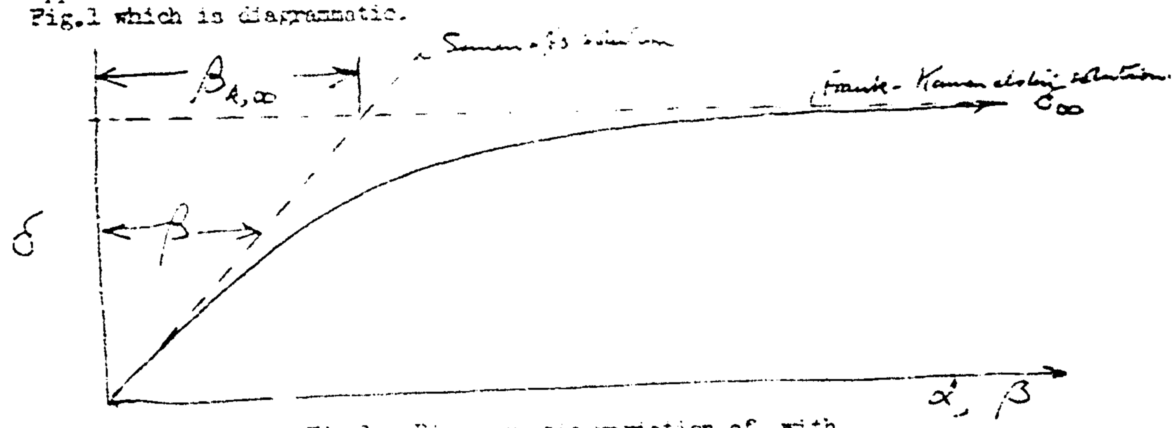

Fig.1. Diagrammatic variation of with

The line tangential to the solution at zero is Semenoff's solution. i.e. equation 4 and δ_∞ is Frank Kamenetski's[2] for $\alpha \rightarrow \infty$. Their intersection determines the effective transfer coefficient as defined by Frank Kamenetski(7) and denoted by β_∞. It has values 2.4. 2.7 and 3.0 for the three configuration k = o, 1 and 2. We now wish to find a value for $\beta (< \beta_\infty)$ so that inserted into equation 4 it gives δ for any value of α. This can then be utilised for approximate methods in transient problems.

First approximate method

The first of two methods is an extension of a device used by Frank kamenetski(7). The approximate equation is

$$-(1+k)\beta.\theta = \frac{d\theta}{d\tau} - \delta.e^{\theta} \qquad \text{......(5)}$$

For an inert solid the equation becomes the quasi-stationary approximation to the ordinary heat conduction problem, which can readily be solved. We have therefore to solve equation 1 with δ zero the boundary conditions 2 and 4 and a suitable initial condition, which for convenience we choose as $\theta = \theta_1$ at t = o. For the sphere the solution is(9)

$$\theta = 2\alpha\theta_1 \sum_{n=1}^{\infty} e^{-\tau a_n^2} \frac{\left(a_n^2 + (\alpha-1)^2\right) \sin z . a_n . \sin a_n}{a_n^2\left(a_n^2 + \alpha(\alpha-1)\right)}$$

where a_n is solution of

$$a_n \cot a_n + \alpha - 1 = 0 \qquad \text{......(6)}$$

However, all we require is the term which is exponential in time as τ tends to infinity. Only the first term (n = 1) is important and this satisfies

$$-a_1^2 . \theta = \frac{d\theta}{d\tau} \qquad \text{......(7)}$$

so that if we compare equation 7 with equation 5 we have

$$3\beta_2 = a_1^2 \qquad \text{......(8)}$$

Frank Kamenetski used the boundary condition $\alpha \to \infty$ for which a_1 equals π which from equations 4 and 8 gives δ_c equal to 3.64 compared with 3.32 for the exact solution (with the Arrhenius term approximated by the exponential). a_1 can readily be obtained from tabulated solutions of equation (6) for any value of α . Hence from equation (8) β_2 is obtained and from (4) δ is obtained. Similarly, for the cylinder, using the solution for conduction in an infinite cylinder(10) we obtain β_1 from

$$2\beta_1 = b_1^2 \qquad \text{......(9)}$$

where b_1 is the first root of

$$b_1 J_1(b_1) = \alpha J_0(b_1) \qquad \text{......(10)}$$

where J_0 and J_1 are Bessel functions of the first kind of order zero and unity. Similarly for the slab

$$\beta_0 = c_1^2 \qquad \text{......(11)}$$

where(11) c_1 is the first root of

$$c_1 \tan c_1 = \alpha \qquad \text{......(12)}$$

As $\alpha \to c$ it can be readily shown that

$$a_1 \to \sqrt{3\alpha}$$
$$b_1 \to \sqrt{2\alpha}$$
$$c_1 \to \sqrt{\alpha}$$

so that from equation (8), (9) and (11) we have

$$\beta_k \to \alpha$$

where $\alpha \to 0$

which satisfies equation 4. Curves of δ as a function of α using these approximations are shown in Fig.2.

The second approximation method

The second approximation is to put θ equal to θ_o on the right-hand side of equation 1 where θ_o is the value of the maximum temperature at zero Z. We can now solve the transient and steady state equation and we shall used the steady state solution to obtain the value of β. Equation 1 can now be integrated in the steady state to give the distribution

$$\theta = \theta_o - \frac{\delta e^{\theta_o} z_1^2}{2(1+k)} \qquad \text{......(13)}$$

Now this gives critical values of δ for infinite α of $\frac{2(1+k)}{e}$ i.e. 0.74, 1.47 and 2.2 instead of 0.88, 2.0 and 3.32 for the three values of k. The correct values for infinite α would be obtained from a distribution

$$\theta = \theta_o - \frac{\delta e^{\theta_o} z_1^{\beta_\infty}}{\beta_\infty(1+k)} \qquad \text{......(14)}$$

For the boundary condition equation (3) and from equation (14) we obtain the critical condition as

$$\theta_o = 1$$
$$\delta_c = \frac{(1+k)}{\left(\frac{1}{\beta_\infty} + \frac{1}{\alpha}\right)e} \qquad \text{......(15)}$$

Comparing (4ii) and (15) we choose for the effective transfer coefficient

$$\frac{1}{\beta} = \frac{1}{\beta_\infty} + \frac{1}{\alpha} \qquad \text{......(16)}$$

a simple additive relation quoted by Gray and Harper[3]. The terms α & β are ratios of a surface transfer coefficient H to an internal resistance λ/r so the above formula may be regarded as the addition of real and hypothetical resistances, surface ones in parallel, or internal ones in series.

Values of δ calculated this way are shown in Fig. 2.

The critical surface temperature θ_S is obtained from equations (14) and (15) as

$$\theta_S = \theta_o - \frac{\delta e^{\theta_o}}{\beta_\infty(1+k)} = \frac{\beta_\infty}{\alpha + \beta_\infty}$$

which is compared in Fig. 3. with the exact solution to equations 1, 2 and 3.

While the effective transfer coefficient β is an approximation which is satisfactory for predicting δ and also θ_S it does not help in assessing θ_o the maximum temperature which varies between 1 and 1.61 because this approximate method is based on a distortion of the temperature distribution and gives θ_o equal to unity at the critical state. Indeed δ_c is generally less sensitive to approximations than is θ_c. For example if the coarse approximation of

$$e^{\theta_o} \approx 1 + 1.72\theta$$

is employed we obtain

$$(1+k)\beta.\theta_o = \delta(1 + 1.72\theta_o)$$

$$\text{i.e.} \quad \delta < \frac{(1+k)\beta}{1.72}$$

which is correct to 60 per cent. However, the corresponding value of θ_o is infinite and the model has broken down qualitatively.

If the approximation of $(1+k)\beta\theta$ is used for $\nabla^2\theta$ we can use it for transient states below the critical where the temperature distribution is more uniform than it is at the critical. In transient states where $\delta > \delta_c$ the distribution may be less uniform and the approximation would be accordingly less valid. However, the conduction term is of order of magnitude θ while the rate of generation of heat is of order δe^{θ} so that as δ increases the conduction term becomes less important than the generation and capacity terms.

The error in making the exponential approximation to the Arrhenius term is obtained from the exact equation.

$$e^{-\frac{E}{RT}} = e^{-\frac{E}{RT_o}} . e^{\theta} . \left\{ e^{-\frac{RT_o^2\theta}{ET}} \right\}$$

By treating the term in brackets as unity we have in fact incurred an error of the magnitude $e^{-\frac{RT_o^2\theta^2}{ET}}$ in δ.

Taking θ as 1.61 (for a sphere) $T = T_o$ and $\frac{E}{RT_o}$ as 25 we find the factor $e^{-\frac{RT\theta^2}{E}}$ to be about 0.88 so that we have underestimated δ by about 10%. It follows that the approximation based on heat conduction theory for an inert material (the upper approximation in Fig.2) may be more accurate than it in fact appears because the 'exact' theory gives a slightly low value. This method can be employed for more complicated shapes(7).

For symmetrical materials equation (16) is a simpler relation than those given by the roots of equations (8), (10) and (12) and in practice is likely to be equally as good, though giving too low a value for δ whereas the others give too high a value.

The use of any of these formulae enables one to discuss simple transient self heating or thermal explosion problems without the necessity of postulating some artificial transfer coefficient unrelated to the real conditions of the problem.

References

(1) Semenoff, N.N. Z.Phys. Chem. 42, 1928, 571.

(2) Frank Kamenetskii, D.A. Zhur.Fiz.Khim 13 (1939) 738.

(3) Gray, P. and Harper, M.J. The 7th International Symposium on Combustion, Oxford 1958.

(4) Allen, A.O., Rice. O.K.. J. Amer, Chem. Soc. 1935 57 310.

(5) Rice. O.K., Allen. A.O. and Cambell, H.C. ibid 1935 57 2212.

(6) Rice, O.K., J. Chem. Phys. 1940 8 727.

(7) Frank-Kamenetskii. D.A. "Diffusion and heat exchange in Reaction Kinetics". 1947. (Translation by N. Thon, Princeton University Press, 1955).

(8) Thomas, P.H. Trans Farady Soc. 1958 54 60.

(9) Carslaw. H.S. and Jaegar. J.C. Conduction of Heat in Solids. 1947. O.U.P. p.203.

(10) ibid p.176.

(11) ibid p.99.

(12) Gray, P. and Harper. M.J. (In the press).

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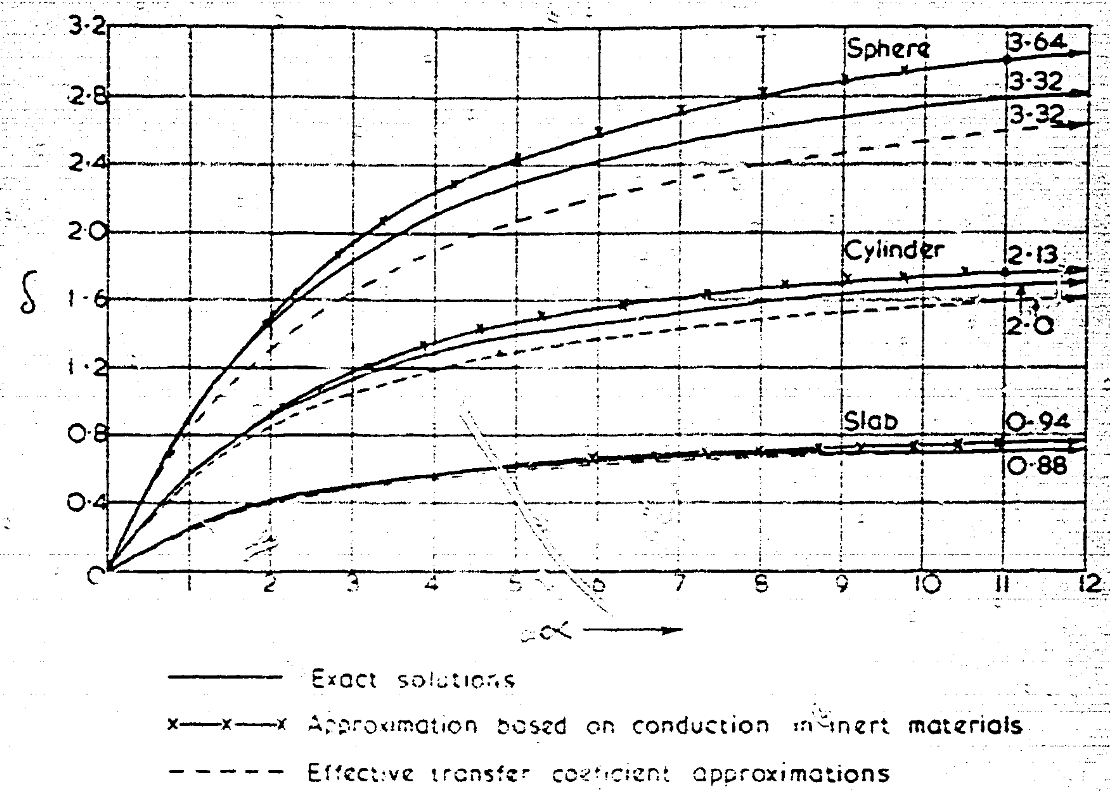

FIG. 2 EXACT AND APPROXIMATE CRITICAL VALUES OF δ

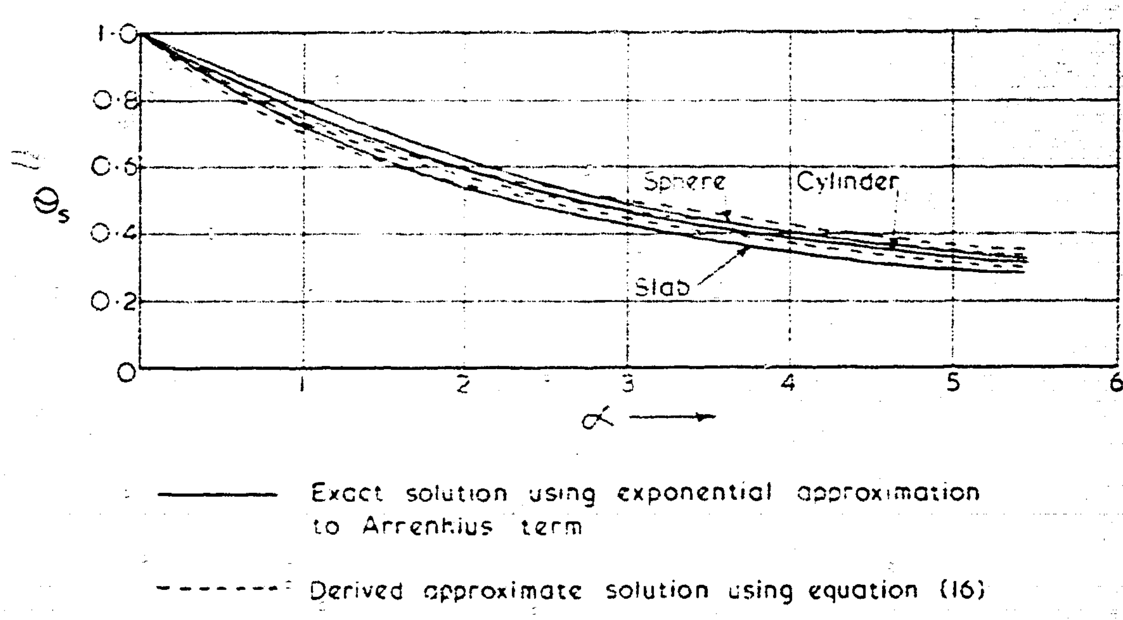

FIG. 3. THE EXACT AND APPROXIMATE DIMENSIONLESS CRITICAL SURFACE TEMPERATURE Θ_s AS A FUNCTION OF α FOR A SPHERE, A CYLINDER AND A SLAB

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