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Thermal Theory of Spontaneous Ignition: Criticality in Bodies of Arbitrary Shape

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THERMAL THEORY OF SPONTANEOUS IGNITION: CRITICALITY IN BODIES OF ARBITRARY SHAPE

By T. BODDINGTON, P. GRAY and D. I. HARVEY
Physical Chemistry Department, The University, Leeds LS2 9JT

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CONTENTS

For an exothermic reaction to lead to explosion, critical criteria involving reactant geometry, reaction kinetics, heat transfer and temperature have to be satisfied. In favourable cases, the critical conditions may be summarized in a single parameter, Frank-Kamenetskii's δ being the best known, but analytical treatments are either confined to idealized geometries, namely, the sphere, infinite cylinder or infinite slab, or require the simplest representations of heat transfer.

In the present paper a general steady-state description is given of the critical conditions for explosion of an exothermic reactant mass of virtually unrestricted geometry in which heat flow is resisted both internally (conductive flow) and at the surface (Newtonian cooling). The description is founded upon the behaviour of stationary-state systems under two extremes of Biot number—that corresponding to Semenov's case ($Bi \to 0$) and that corresponding to Frank-Kamenetskii's case ($Bi \to \infty$); it covers these and intermediate cases.

For Semenov's conditions, the solution is already known, but a fresh interpretation is given in terms of a characteristic dimension—the mean radius R_S. A variety of results for criticality is tabulated.

For Frank-Kamenetskii's conditions, the central result is an approximate general solution for the stationary temperature distribution within any body having a centre. Critical conditions follow naturally. They have the simple form:

$$\left[\frac{q\sigma A \exp\left(-E/\mathbf{R}T_a\right)}{\kappa \mathbf{R}T_a^2/E} R_0^2\right]_{cr} \equiv \delta_{cr}(R_0) = 3F(j),$$

where $F(j)$ is close to unity, being a feeble function of shape through a universally defined shape parameter j, and $\delta_{cr}(R_0)$ is Frank-Kamenetskii's δ evaluated in terms of a universally defined characteristic dimension R_0—a harmonic square mean radius weighted in proportion to solid angle:

$$\frac{1}{R_0^2} = \frac{1}{4\pi}\iint \frac{d\omega}{a^2}.$$

Expressions for the mean radius R_0 have been evaluated and are tabulated for a broad range of geometries. The critical values generated for δ are only about 1% in error for a great diversity of shapes. No adjustable parameters appear in the solution and there is no requirement of an *ad hoc* treatment of any particular geometric feature, all bodies being treated identically. Critical sizes are evaluated for many different shapes.

For arbitrary shape and arbitrary Biot number ($0 < Bi < \infty$) an empirical criterion is proposed which predicts critical sizes for a great diversity of cases to within a few parts per cent.

Rigorous, closely adjacent upper and lower bounds on critical sizes are derived and compared with our results and with previous investigations, and the status of previous approaches is assessed explicitly. For the most part they lack the generality, precision and ease of application of the present approach.

1. Introduction

In a recent review (Gray & Lee 1967*a*) of thermal explosion theory, Gray and Lee discuss the problem of defining criticality for bodies of various shapes in which temperatures vary from point to point, and list the main attempts to attack this problem. Most approaches are based on the parameter δ of Frank-Kamenetskii which was defined originally for the three geometrically simple configurations in which temperature is a function of one coordinate only—the sphere, the infinite cylinder and the infinite slab. For these

$$\delta \equiv \frac{a_0^2 \sigma q E A \exp\left(-E/\boldsymbol{R}T_a\right)}{\kappa \boldsymbol{R} T_a^2},$$

where a_0 is the radius or half-width, and the critical values are known to be 3.32, 2 and 0.88 respectively. Arbitrarily weighted means have been employed to estimate δ_{cr} for spherocylinders but, for compact bodies, most progress has been made in terms of the concept of the equivalent sphere—that sphere of the same material which explodes at the same ambient temperature as the body in question. Previous treatments have been restricted to the simple limiting case of Frank-Kamenetskii (Dirichlet) boundary conditions, which fix the surface temperature at the ambient value (and correspond to infinite Biot number). Additional conspicuous deficiencies prompting the present treatment are the arbitrary nature of the putative equivalences invoked, the poor precision of their results, and their inability to cope with more than a few simple geometries.

Treatments in terms of averaged temperatures (Semenov boundary conditions, zero Biot number) are far simpler. The surface to volume ratio is the only geometrical feature that matters, and it is the purpose of the present paper to build on this, and on those already examined cases in which temperatures vary from point to point, in order to derive analytically a practically useful criterion of almost unrestricted applicability. The feature distinguishing our approach from earlier ones is that it is founded on a general solution (although inexact) of the corresponding heat balance equation, and not on a study of some other physical situation which is amenable to analysis and deemed intuitively to be similar. The results will be compared with a range of previously and newly derived exact results and with previous approximate approaches (some of which appear to contain errors) and finally extended to the generalized boundary conditions where interior, surface and ambient temperatures are all different (arbitrary Biot number).

Among physically understandable consequences is the dominance of the smallest dimensions of a body in determining criticality—harmonic means and harmonic square mean distances being a natural feature of the analysis.

The notation employed is partly novel in order to cope with the more general scope; it is set out in appendix 1.

2. Semenov's boundary conditions—uniform internal temperature

Under Semenov boundary conditions the thermal conductivity of the reactant mass is so great that the internal temperature T is essentially constant throughout the volume V occupied, and exceeds the ambient value T_a. The heat balance equation for the system is thus extremely simple and the criticality problem for arbitrary shapes is a trivial one. The complete solution of the problem is given by Semenov's classical approach (Semenov 1928). A steady state exists if

$$\psi < \psi_{cr} = e^{-1},$$

where

$$\psi = \left(\frac{V}{S}\right)\left(\frac{q\sigma AE \exp(-E/RT_a)}{HRT_a^2}\right),$$

H is the heat transfer coefficient at the surface S and q, σ, A, E are the exothermicity per unit mass, density, pre-exponential factor and activation energy, respectively, of the reactant.

The (Semenov) equivalent sphere (i.e. that sphere of the same reactant which has the same critical temperature when subjected to the same surface heat transfer coefficient) is clearly one of the same volume/surface ratio, i e. with radius given by $R_S = 3V/S$. This result may be given a simple and instructive geometric interpretation: R_S can be written in the form

$$R_S = 3\frac{V}{S} = S^{-1}\iint_S \boldsymbol{a}.\mathrm{d}\boldsymbol{S} = S^{-1}\iint_S l\,\mathrm{d}S = \langle l \rangle_S, \tag{2.1}$$

where $\boldsymbol{a}$ is the radius vector from an origin (which is arbitrarily located inside or outside the surface) to the surface element $\mathrm{d}\boldsymbol{S}$, and l is the length of the perpendicular from the origin onto the plane containing $\mathrm{d}\boldsymbol{S}$ (see figure 1). Thus *the Semenov equivalent sphere radius is the mean distance of the surface from any centre.* An immediate consequence of this is that the body formed from a sphere by completely enclosing it in any (finite or infinite) number of tangent planes is the (Semenov) equivalent of that sphere. If now any number of plane cuts are made in planes lying outside the sphere to remove material from the body, then the resulting body has a Semenov sphere radius greater than that of the original sphere. Practically, this indicates conditions under which removal of 'protuberances' leads to an increased explosion hazard (i.e. reduced critical temperature) despite reduction in total mass.

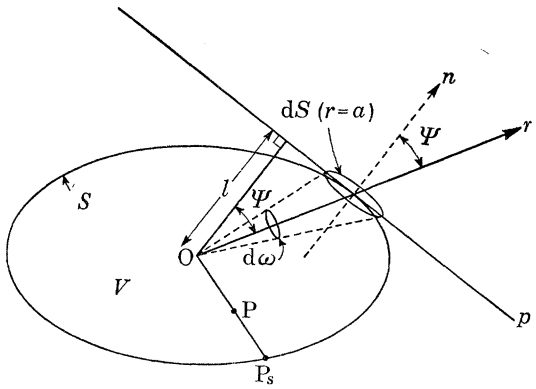

FIGURE 1. Some geometric features of a surface. V reactant mass, S its surface, dS element of surface, p tangent plane of dS, n the normal of dS, O body centre, dω solid angle subtended at O by dS, r radius vector. The coordinate ρ of the general point P is defined to be OP/OP$_S$.

Results for some simple shapes. These are set out in table 1. Clearly there is no difficulty in finding V and S, and thus R_S for any shape—although it may involve quadrature (see appendix 2(*a*)). R_S is well behaved in the sense that it remains finite so long as any one characteristic dimension remains finite. Physically, of course, we know that extension without limit in one or two directions does not lead to explosion i.e. does not make R_S tend to infinity. R_S has the nature of a harmonic mean dimension, so that it is the *smallest* dimension of the body which dominates the Semenov sphere radius. This is well illustrated by the expression for the rectangular brick $(2a \times 2b \times 2c)$:

$R_S^{-1} = \frac{1}{3}(a^{-1}+b^{-1}+c^{-1})$. This result suggests that an approximate value of the *squared* Frank-Kamenetskii sphere radius is some form of harmonic mean of the squared characteristic distances of the body, and prompts the analysis of the next section.

TABLE 1. THE RECIPROCAL SEMENOV RADIUS, $R_S^{-1} = S/3V$, FOR SOME SIMPLE GEOMETRIES

geometry	R_S^{-1}
∞ slab, thickness = $2a$	$\frac{1}{3}a^{-1}$
∞ cylinder, radius a; ∞ square rod, side $2a$	$\frac{2}{3}a^{-1}$
sphere, radius a; cube, side $2a$; equicylinder, height = diameter = $2a$	a^{-1}
rectangular brick ($2a \times 2b \times 2c$)	$\frac{1}{3}(a^{-1}+b^{-1}+c^{-1})$
∞ rectangular rod ($2a \times 2b$)	$\frac{1}{3}(a^{-1}+b^{-1})$
cylinder, length $2d$, radius a	$\frac{1}{3}(2a^{-1}+d^{-1})$
as above, capped by hemispheres	$[a+\frac{1}{2}(a^{-1}+d^{-1})^{-1}]^{-1}$
equiconvex lens, thickness $2l$, aperture $2c$, $\mu = c/l-1$	$l^{-1}\dfrac{1+\mu+\frac{1}{2}\mu^2}{1+\frac{3}{2}\mu+\frac{3}{4}\mu^2}$
spheroid, semi-axes a, b; $a < b$, excentricity $\nu = b^{-1}(b^2-a^2)^{\frac{1}{2}}$	Ca^{-1}, where:
oblate: $C = \dfrac{1}{2}\left[1+\dfrac{1-\nu^2}{2\nu}\ln\left(\dfrac{1+\nu}{1-\nu}\right)\right]$	$\frac{1}{2} < C < 1$
prolate: $C = \dfrac{1}{2}\left[\sqrt{(1-\nu^2)}+\dfrac{\sin^{-1}\nu}{\nu}\right]$	$\frac{1}{4}\pi = 0.785 < C < 1$

For further results see appendix 2(*a*).

3. DISTRIBUTED TEMPERATURES: FRANK-KAMENETSKII'S BOUNDARY CONDITIONS

3(*a*). *Introduction*

The problem of describing the temperature distribution and hence of deriving critical conditions for explosion becomes extremely complicated when Semenov's boundary conditions no longer apply. For then there is no longer a single temperature which describes the system and (in general) the temperature is a point function depending on three spatial coordinates. Symmetry properties of the reactant mass may permit a description in terms of only one or two spatial coordinates. The geometries describable in terms of only a single spatial coordinate, i.e. the infinite slab, the infinite circular cylinder and sphere (which for convenience we shall call class A geometries), have been extensively studied (Frank-Kamenetskii 1955; Chambré 1952; Chandrasekhar & Wares 1949; Boddington & Gray 1970; Merzhanov & Dubovitskii 1958) and the nature of their temperature profiles and of their critical conditions is well known. The tractability of the one-dimensional problems is a consequence of the simplicity of the equation describing local heat balance—an *ordinary* second-order differential equation. For geometries other than class A we must solve a *partial* second-order differential equation in two or three independent variables. For realistic dependences of reaction rate on temperature the differential equation is, moreover, nonlinear, and thus the method of separation of variables is not applicable. No general analytic solutions are known of the intractable equations describing *particular* geometries of interest other than class A. It would seem that a *general* solution is beyond reach. Numerical solutions may be carried out in a straightforward manner for a particular shape and boundary condition, but the identification of the critical conditions even for a single geometric shape requires extensive computation. It seems unlikely that a numerical approach can yield much general insight into the problem.

Because of the very considerable difficulties outlined above we proceed, in this section, by using a general—although inexact—solution of the basic equation based on (and indeed reducing to) the known exact solutions for class A geometries. A number of features of our approximate solution lend it plausibility, but it is extremely difficult to give a general *a priori* discussion of its precision. Ultimately our approach is justified by the good agreement between its results and known exact results for a wide range of geometries. It is inherent in our approach that the body under discussion should possess a centre of symmetry (see however § 8). Further, we would only assert that our solutions are satisfactory for reactant masses bounded by surfaces that are everywhere convex outwards. The latter two conditions apart, our solution is entirely general. No *ad hoc* treatment of particular geometric features is required and no adjustable parameters appear in the solution.

3(*b*). *Local conservation of energy*

In general our systems are completely described by the equations expressing local conservation of energy

$$\operatorname{div}\mathbf{grad}\, T + q\sigma A \exp(-E/\mathbf{R}T) = 0 \quad \text{in } V, \tag{3.1}$$

$$\kappa\, \mathrm{d}T/\mathrm{d}n + H(T - T_\mathrm{a}) = 0 \quad \text{on } S. \tag{3.2}$$

Here κ, σ, q are the thermal conductivity, density and exothermicity per unit mass of the reactant, $A\exp(-E/\mathbf{R}T)$ is its fractional rate of disappearance, and T is the local absolute temperature. V denotes the volume occupied by the reactant, S its surface, T_a the ambient temperature to which it is subjected, H is the surface heat transfer coefficient and n is directed along the outward normal to the surface (see figure 1).

If the Biot number, $Bi = HR_\mathrm{S}/\kappa$, tends to zero the temperature within V becomes uniform, i.e. we have the Semenov régime discussed in § 2. If, however, Bi tends to infinity the boundary condition (3.2) degenerates to

$$T = T_\mathrm{a} \quad \text{on } S, \quad Bi \to \infty. \tag{3.3}$$

We postpone a discussion of the complicated general case (equations (3.1), (3.2)) until § 5, and consider first the solution of equations (3.1), (3.3), which correspond to the Frank-Kamenetskii (Dirichlet) régime.

3(*c*). *Construction of an approximate general solution for the Frank-Kamenetskii régime*

We consider this problem in the usual Frank-Kamenetskii (1955) approximation

$$\exp(-E/\mathbf{R}T) \to \exp(-E/\mathbf{R}T_\mathrm{a})\, \mathrm{e}^{\theta},$$

where

$$\theta = E(T - T_\mathrm{a})/\mathbf{R}T_\mathrm{a}^2.$$

Equations (3.1), (3.3) then become

$$\operatorname{div}\mathbf{grad}\,\theta + \gamma\, \mathrm{e}^{\theta} = 0 \quad \text{in } V, \tag{3.4}$$

$$\theta = 0 \quad \text{on } S, \tag{3.5}$$

where

$$\gamma = q\sigma AE \exp(-E/\mathbf{R}T_\mathrm{a})/\kappa\mathbf{R}T_\mathrm{a}^2 \tag{3.6}$$

has the dimensions of $(\text{length})^{-2}$. For the highly symmetric class A geometries, (3.4) and (3.5) may be written in the simple reduced form

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}\rho^2} + \frac{j}{\rho}\frac{\mathrm{d}\theta}{\mathrm{d}\rho} + \delta(a_0)\, \mathrm{e}^{\theta} = 0, \tag{3.7}$$

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$$\theta|_{\rho=1} = 0, \quad (3.8)$$

$$\left.\frac{d\theta}{d\rho}\right|_{\rho=0} = 0, \quad (3.9)$$

where (3.9) corresponds to a maximal central temperature due to the symmetry, j is a dimensionless number denoting the shape ($j = 0, 1, 2$ for the slab, cylinder and sphere) and δ is the well-known Frank-Kamenetskii parameter based on the radius or half-width a_0:

$$\delta(a_0) = \gamma a_0^2. \quad (3.10)$$

The variable ρ is usually interpreted as r/a_0, where r is the distance from the central plane, axis or centre respectively. Below we require a more general definition and we shall use the following:

$\rho(\mathrm{P})$ is the distance of a general point P from the centre of the body O, divided by the distance from the centre O to the surface *S in the direction* ***OP*** (see figure 1).

3 (*c*) (i). *A unified solution for class A geometries*

We first consider a formal parametric solution of (3.7) to (3.9). This is generated by means of the substitution of

$$\theta_0 - \theta = 2 \ln X(\rho) \quad (3.11)$$

into (3.7), where θ_0 denotes $\theta(\rho = 0)$, the dimensionless temperature excess at the origin O. A comparison of the coefficients of ρ^2 gives

$$X(\rho) = \sum_{n=0}^{\infty} b_n (y\rho^2)^n, \quad (3.12)$$

where y is a parameter which must satisfy the boundary condition (3.8):

$$\theta_0 = 2 \ln X_1, \quad (3.13)$$

$$X_1 \equiv X(\rho = 1) = \sum_{n=0}^{\infty} b_n y^n, \quad (3.14)$$

δ is given by

$$\delta(a_0) = 12 \, . \tfrac{1}{3}(j+1)\, y X_1^{-2}, \quad (3.15)$$

and the coefficients $b_n(j)$ are to be found from the recurrence relation

$$(n+1)(2n+j+1)\, b_{n+1} = \sum_{s=0}^{n} (n-s)(4s-2n+3-j)\, b_{s+1} b_{n-s} \quad (n \geqslant 1); \quad (3.16)$$

using $b_0 = b_1 = 1$. Equations (3.11) to (3.16) constitute a unified statement of the well-known solutions (Frank-Kamenetskii 1955; Chambré 1952; Chandrasekhar & Wares 1949; Boddington & Gray 1970; Merzhanov & Dubovitskii 1958) for class A geometries in terms of the parameter y. It should be noted that the leading coefficients b_0, b_1 are independent of j (and thus of shape) and that subsequent coefficients $b_2, b_3, \ldots,$ are small, being zero for the infinite cylinder ($j = 1$). Thus

$$b_0 = b_1 = 1; \quad b_2 = \frac{1-j}{2(j+3)}; \quad b_3 = \frac{(j-1)(3j-1)}{6(j+3)(j+5)}.$$

These results have the consequence that the relation $\theta = \theta(\rho, \theta_0, j)$ generated by (3.11) to (3.16) depends very feebly on shape notwithstanding the three very different and extreme geometries under consideration. In fact, manipulating (3.11) to (3.16), we may write

$$\theta = \theta_0(1-\rho^2)\left\{1 - \tfrac{1}{2}\left(\frac{j+1}{j+3}\right)\rho^2\theta_0 + O(\rho^4\theta_0^2)\right\}, \quad (3.17)$$

where the coefficient $(j+1)/2(j+3)$ takes the values 0.167, 0.250 and 0.300 for class A geometries. Since $\rho^2\theta_0 \lesssim 1$ in all cases of interest, (3.17) illustrates well the feeble dependence of $\theta = \theta(\theta_0, \rho)$ on shape.

3 (*c*) (ii). *The general solution for arbitrary geometries*

Since an exact analytical solution of the general problem is not forthcoming we are compelled to seek a satisfactory approximation. Guided by our unified solution of the problem for class A geometries, we assume that equations (3.11) to (3.14) and (3.16) constitute an approximate solution $\theta = \theta(\theta_0, \rho, j)$ of equations (3.4) and (3.5) for a body of any shape† possessing a centre of symmetry.‡ This plausible hypothesis demands justification *a posteriori*. In order to use it we must define the shape parameter j for a general body in a suitable manner. A satisfactory definition must involve a *complete* specification of the body (not merely the few principal dimensions specified in earlier approaches). This requirement is met by defining the surface S in the form

$$r = a(\Theta, \phi) \quad \text{on } S, \tag{3.18}$$

where (r, Θ, ϕ) are the usual spherical-polar coordinates with the origin at the body centre O, and $a(\Theta, \phi)$ is a specified function for a given geometry. The definition of j must be such that j depends continuously on the parameters of the function $a(\Theta, \phi)$, must give the correct results for the class A geometries and be applicable to a general shape (in particular, must treat all directions (Θ, ϕ) equivalently). Once these rather strong restrictions have been satisfied, any residual arbitrariness in the definition should not be important since, because the solutions $\theta = \theta(\theta_0, \rho, j)$ depend feebly on the shape parameter j for the three very extreme geometries of class A, we may reasonably expect that this will also be true of the intermediate cases. A convenient definition meeting all our stipulations is given by

$$\left.\begin{aligned} j &= 3\chi - 1, \\ \chi &= R_0^2 R_S^{-2}, \\ \frac{1}{R_0^2} &= \frac{1}{4\pi}\iint \frac{d\omega}{a^2}. \end{aligned}\right\} \tag{3.19}$$

Here R_0^{-2} is the value of $a^{-2}(\Theta, \phi)$ averaged § over 4π steradians. Since R_S and R_0 are defined and finite for all bodies with a finite dimension we see that j is defined and finite for all bodies.‖ For *convex* bodies the shape parameter defined by (3.19) has values lying between 0 (the infinite slab) and 4.187 (the regular tetrahedron).

The length R_0, which we may conveniently refer to as the *mean radius*, proves to be an excellent first approximation to the Frank-Kamenetskii equivalent sphere radius, R_{FK}, and arises naturally from a consideration of the dependence of θ_0 on γ. In fact our solution (3.11), (3.12) has the form $\theta = \theta(\theta_0, \rho, j)$ and is as yet incomplete, in that it remains to relate θ_0 to the physical parameter γ. It should be noted that (3.15), which involves $\delta(a_0)$, is not invoked in our solution, nor can it be, since a_0 is not defined for bodies other than class A. Here lies the principal obstacle to using

† Subsequently we find we must restrict our treatment to starshaped bodies (those having the property that a ray in any direction through the centre meets the surface only once).

‡ I.e. a point at which the symmetry of the body compels zero temperature gradient in three non-coplanar directions, so that **grad** $\theta = 0$ and θ is stationary. This point may be an inversion centre or the unique point defined by the intersection of planes and/or axes of symmetry.

§ The factor $1/4\pi$ in the definition of R_0^{-2} serves to normalize the integral to produce a mean value for a^{-2}, thus ensuring that for a sphere of radius a_0 we have $R_0 = a_0$.

‖ In order that a be a single valued function of Θ and ϕ, we must in fact restrict our attention to bodies which are stellate, centre O.

a generalized Frank-Kamenetskii parameter δ. For the class A geometries there is an 'obvious' dimension a_0 that may be combined with γ to give an 'obvious' dimensionless parameter, $\delta(a_0) = \gamma a_0^2$. For other geometries the choice of a_0 is arbitrary, so that (3.15) cannot be generalized directly. This difficulty is resolved automatically below in deriving the relation $\gamma(\theta_0)$.

We 'normalize' our solution $\theta = \theta(\theta_0, \rho, j)$ by substituting it in the basic equation (3.4). (Equations (3.11) and (3.13) automatically satisfy the boundary condition (3.5).) The substitution is conveniently effected at the body centre O, giving

$$\gamma\, e^{\theta_0} = \gamma X_1^2 = -\operatorname{div}\mathbf{grad}\,\theta = -\lim_{V^1\to 0}\left\{\frac{1}{V^1}\iint \mathbf{grad}\,\theta\,.\,\mathrm{d}\boldsymbol{S}^1\right\}, \tag{3.20}$$

where V^1 is the volume enclosed by a control surface S^1 surrounding the origin. Letting this surface be a sphere† of radius $r_0 (r_0 \to 0)$ and noting that

$$\mathbf{grad}\,\theta\,.\,\mathrm{d}\boldsymbol{S}^1 = \frac{r_0^2}{a}\frac{\partial\theta}{\partial\rho}\,\mathrm{d}\omega,$$

$$\lim_{r_0\to 0}\left(\frac{\partial\theta}{\partial\rho}\right) = -4y\left(\frac{r_0}{a}\right), \quad \text{(from (3.11) and (3.12))}$$

and

$$V^1 = \tfrac{4}{3}\pi r_0^3,$$

we find that (3.20) reduces to

$$\gamma X_1^2 = 12y\,\frac{1}{4\pi}\iint_S a^{-2}\,\mathrm{d}\omega = 12yR_0^{-2}, \tag{3.21a}$$

or

$$\delta(R_0) \equiv \gamma R_0^2 = 12X_1^{-2}\,y(X_1, j). \tag{3.21b}$$

Since X_1 equals $\exp(\frac{1}{2}\theta_0)$ and $y(X_1, j)$ is known from (3.14), we see that (3.21 *a*) relates γ and θ_0 (without assigning special prominence to any single dimension). Similarly, (3.21 *b*) relates θ_0 to a δ based on a dimension R_0 which arises directly from the heat balance equation and which is unambiguously and systematically defined. Equation (3.21 *b*) is the required generalization of (3.15), which itself applies only to class A geometries, for which we have $R_0^{-2} \equiv \frac{1}{3}(j+1)\,a_0^{-2}$ (see appendix 2 (*b*)). Our approximate general solution, given by the set of equations (3.11) to (3.14), (3.16), (3.19) and (3.21), is now complete. By omitting mere definitions we can summarize it as follows:

$$\left.\begin{aligned} \theta &= \theta_0 - 2\ln\left[\sum_{n=0}^{\infty} b_n(j)\,(y\rho^2)^n\right],\\ e^{\frac{1}{2}\theta_0} &= X_1 = \sum_{n=0}^{\infty} b_n(j)\,y^n,\\ \delta(R_0) &= 12X_1^{-2}\,y(X_1, j). \end{aligned}\right\}\text{general solution.} \tag{3.22}$$

3 (*c*) (iii). *Merits and limitations of the general solution*

Although it is not possible to conduct a thorough analysis of the precision of (3.22) for arbitrary shapes, some consideration of its advantages and disadvantages is appropriate:

(*a*) It is an extremely simple, compact general solution in terms of the parameter y. When values of y and j are assigned, $\delta(R_0)$ and $\theta(\rho)$ are readily calculated.

(*b*) The geometric properties of shape and scale are embodied in only two parameters j and R_0, these being universally defined.

† Because our solution $\theta(\theta_0, \rho, j)$ is not exact for arbitrary geometry, the result of our normalization depends slightly on the shape of the control surface. The choice of the sphere is not only plausible and convenient but also generates the most accurate results.

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(*c*) The solution (3.22) is an exact formal solution for the three very disparate geometries infinite slab, infinite cylinder and sphere, its simple form notwithstanding.

(*d*) The solution involves only one reduced coordinate $\rho = r/a(\Theta, \phi)$. This fact greatly (and indeed crucially) simplifies the algebra and implies that the isotherms, $\theta = \text{const.}$, correspond to $\rho = \text{const.}$ or to $r = \text{const.} \times a(\Theta, \phi)$, i.e. are geometrically similar to the outer surface. While this is an acceptable first approximation in general (it is exact for class A), it implies in turn that surfaces with discontinuities have discontinuous isotherms, whereas our elliptical basic equation does not admit the propagation of such discontinuities. This is not a grave deficiency since we are principally concerned not with the detailed local behaviour of the temperature but with the overall property of criticality. The pathological behaviour at the origin (in particular) of the temperature distribution (3.22) corresponding to a body with surface discontinuities is disturbing, but does not demand special attention in our analysis.

(*e*) The solution automatically ensures that the maximal temperature is achieved at the body centre since there $\partial\theta/\partial r \to 0$ *for all directions* (Θ, ϕ).

(*f*) In general the equation of local heat balance is only satisfied *exactly* at the centre O. To consider this we note that (3.22) is the formal solution of the ordinary differential equation

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}\rho^2} + \frac{j}{\rho}\frac{\mathrm{d}\theta}{\mathrm{d}\rho} + \tfrac{1}{3}(j+1)\,\delta(R_0)\,\mathrm{e}^{\theta} = 0; \quad \text{in } V, \tag{3.23}$$

subject to the boundary conditions

$$\theta = 0 \quad \text{at} \quad \rho = 1 \quad (\text{i.e. } r = a(\Theta, \phi), \quad \text{i.e.} \quad \text{on } S), \tag{3.24}$$

and

$$\mathrm{d}\theta/\mathrm{d}\rho = 0 \quad \text{at} \quad \rho = 0. \tag{3.25}$$

Although (3.24) and (3.25) are the correct boundary conditions, (3.23) is not the correct heat balance equation (see (3.4)). However, for the class A geometries (3.23) reduces identically to (3.7) even though great extremes of shape are involved. Since, additionally, the correct heat balance equation (3.4) is satisfied for all shapes at the centre (equation (3.21)), we expect local heat imbalance to be small.

(*g*) A comparison of the critical conditions generated by our approximate solution and of those found by exact computation is given in § 4 (*a*). The close agreement for a wide range of geometries is encouraging and ultimately constitutes a justification of the use of our fundamental hypothesis. Additional support is lent by the fact that our results for an even wider range of geometries lie within rigorously derived bounds (see § 6).

(*h*) There are difficulties associated with the convergence of the infinite series appearing in (3.22). These are circumvented in the next section by using finite reversions of the series.

4. Nature of the general solution for Frank-Kamenetskii boundary conditions: critical conditions for explosion in bodies of arbitrary shape

In this section we examine the major features of our approximate general solution (3.22) for the internal temperature distribution, find the critical conditions for explosion by demonstrating that no steady-state solution exists if $\delta(R_0)$ exceeds a certain value (which depends feebly upon shape), and thus derive a simple expression for the radius of the equivalent Frank-Kamenetskii sphere, which may be compared with the corresponding Semenov radius.

4 (*a*). *Dependence of temperature profile on shape and thermochemical parameters: critical conditions for explosion*

The general parametric solution (3.22) may be used directly to generate solutions (the same in all directions) of the form

$$\theta = \theta(\rho, \delta(R_0), j).$$

To this end the infinite summations in (3.22) may be truncated after $n = 5$ with very small resultant error. A very simple and remarkably accurate alternative is to use the second-order reversion: $y\rho^2 = (X-1)[1-b_2(X-1)]$. The shapes of the profiles for all shape parameters j are essentially the same—they are roughly parabolic with a maximum at the centre and zero at the edge. If $j > 1$ then an inflexion in the profile is observed near the surface ($\rho = 1$) if $\delta(R_0)$ is sufficiently close to its critical value $\delta_{cr}(R_0)$. The profiles are well illustrated by the cases $j = 0, 1, 2$ which have been discussed in detail by Boddington & Gray (1970).

The variation of the self-heating effect with scale or with ambient temperature may conveniently be represented by the relation $\theta_0(\delta[R_0])$, given parametrically by (3.22). When $\delta(R_0)$ is small we have $\theta_0 \to 0$ and

$$\left.\frac{\mathrm{d}\delta(R_0)}{\mathrm{d}\theta_0}\right|_{\delta\to 0} \to 6 \quad \text{for all geometries.}$$

As δ increases above zero the gradient $\mathrm{d}\delta/\mathrm{d}\theta_0$ diminishes steadily so that δ eventually attains a maximum value $\delta_{cr}(j)$.† This maximum represents the critical régime, i.e. corresponds to the greatest value of δ for which a steady state is possible. The gradient of $\delta(\theta_0)$ is, from (3.22), given by

$$\frac{\mathrm{d}\ln\delta}{\mathrm{d}\theta_0} = \frac{1}{2}\frac{\mathrm{d}\ln y}{\mathrm{d}\ln X_1} - 1, \tag{4.1}$$

so that at criticality we have‡

$$\frac{\mathrm{d}\ln X_1}{\mathrm{d}\ln y} \equiv -\frac{1}{4}\left.\frac{\mathrm{d}\theta}{\mathrm{d}\rho}\right|_{\rho=1} = \tfrac{1}{2}, \tag{4.2}$$

or

$$\sum_{n=1}^{\infty}(2n-1)\, b_n y^n = 1. \tag{4.3}$$

The critical values of δ and θ_0 are to be found by substituting the critical value of y given by (4.3) into (3.22). Although this may be done precisely, the results are greatly simplified and very little error is introduced (see below) by making use of the second-order reversion of (3.14):

$$y = (X_1-1)[1-b_2(X_1-1)]. \tag{4.4}$$

With this approximation $\delta(\theta_0)$ has the simple form

$$\delta(R_0) = 12X_1^{-2}(X_1-1)[1-b_2(j)(X_1-1)]; \quad X_1 = \mathrm{e}^{\frac{1}{2}\theta_0} \tag{4.5}$$

$$\frac{\mathrm{d}\delta}{\mathrm{d}\theta_0} = 6X_1^{-2}\left[\frac{(j+7)-4X_1}{j+3}\right]. \tag{4.6}$$

Thus the following very simple relations hold at criticality:

$$X_{1,\mathrm{cr}} = \tfrac{1}{4}(j+7), \tag{4.7}$$

$$\theta_{0,\mathrm{cr}} = 2\ln[\tfrac{1}{4}(j+7)], \tag{4.8}$$

† When the argument of δ is not made explicit it is to be understood to be R_0, i.e. $\delta = \gamma R_0^2$.

‡ This result gives $-\mathrm{d}\theta/\mathrm{d}\rho|_{\rho=1} = 2$ at criticality for all directions (Θ, ϕ) and for all shapes, thus generalizing a result due to Enig (1966).

$$y_{\rm cr} = \tfrac{1}{32}(j+3)(j+7), \tag{4.9}$$

$$\delta_{\rm cr}(R_0) = 3F(j), \tag{4.10}$$

$$F(j) = (2j+6)/(j+7), \tag{4.11}$$

$$\delta_{\rm cr} = 6(1-{\rm e}^{-\frac{1}{2}\theta_0}). \tag{4.12}$$

The critical values of the parameters depend solely on the shape parameter j.

The form of $\delta(\theta_0)$ given by (4.5) is illustrated in figure 2. The region to the right of the critical locus (4.12) corresponds to unstable steady-state solutions. The stable steady-state solutions of physical interest lie to the left of the critical locus. It is clear that the dependence of the sub-critical behaviour on shape is slight.

The error incurred by replacing (3.14) by its second-order reversion (4.4) is small. The greatest

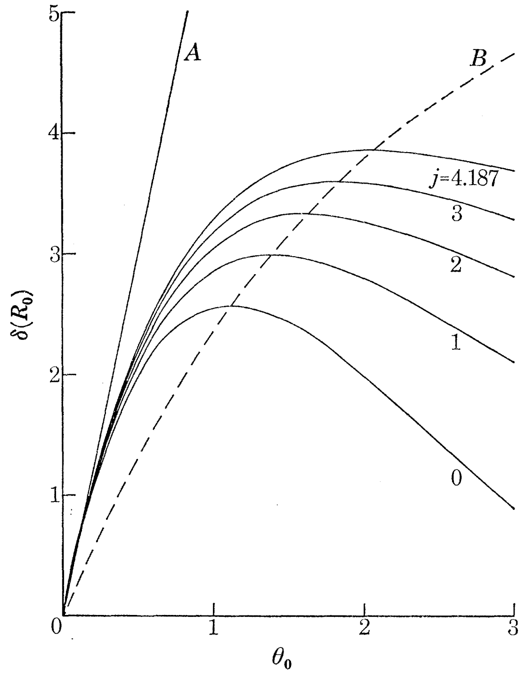

FIGURE 2. Variation of the generalized Frank-Kamenetskii parameter $\delta(R_0) = \gamma R_0^2$ with the reduced central temperature excess θ_0 under Frank-Kamenetskii boundary conditions, according to (4.5). The curves shown cover the entire range of convex geometries ($0 \leqslant j \leqslant 4.187$). A is the low δ asymptote for all geometries: $\delta(R_0) = 6\theta_0$. B is the critical locus given by (4.12). The region between A and B corresponds to stable solutions. To compare this figure with the classical results for slab, cylinder and sphere note that $\delta(a_0) = [(j+1)/3]\,\delta(R_0)$.

TABLE 2. COMPARISON OF $\theta_{0,\,\rm cr}$ AND $\delta_{\rm cr}(a_0)$ DERIVED FROM THE CRITICAL CRITERION (4.7) AND THE EXACT VALUES FOR CLASS A GEOMETRIES

	$\theta_{0,\,\rm cr}$			$\delta_{\rm cr}(a_0)$		
geometry	exact	(4.8)	error (%)	exact	(4.10)	error (%)
∞ slab	1.187	1.119	−6	0.878	0.857	−2
∞ cylinder	1.387	1.387	0	2	2	0
sphere	1.61	1.622	$+\frac{1}{2}$	3.322	3.333	$+\frac{1}{3}$

error for régimes of physical interest occurs at criticality. In table 2 we compare the values of $\theta_{0,\,\mathrm{cr}}$ and $\delta_{\mathrm{cr}}(R_0)$ generated by (3.22) and (4.3) with the values generated by (4.8) and (4.10) for the class A geometries. The results of the former are exact in the Frank-Kamenetskii approximation $(RT_a/E \to 0)$. In view of the small errors involved we shall use (4.4) in all further discussion, with the result that our expressions have especially simple forms deriving from (4.7) to (4.11).

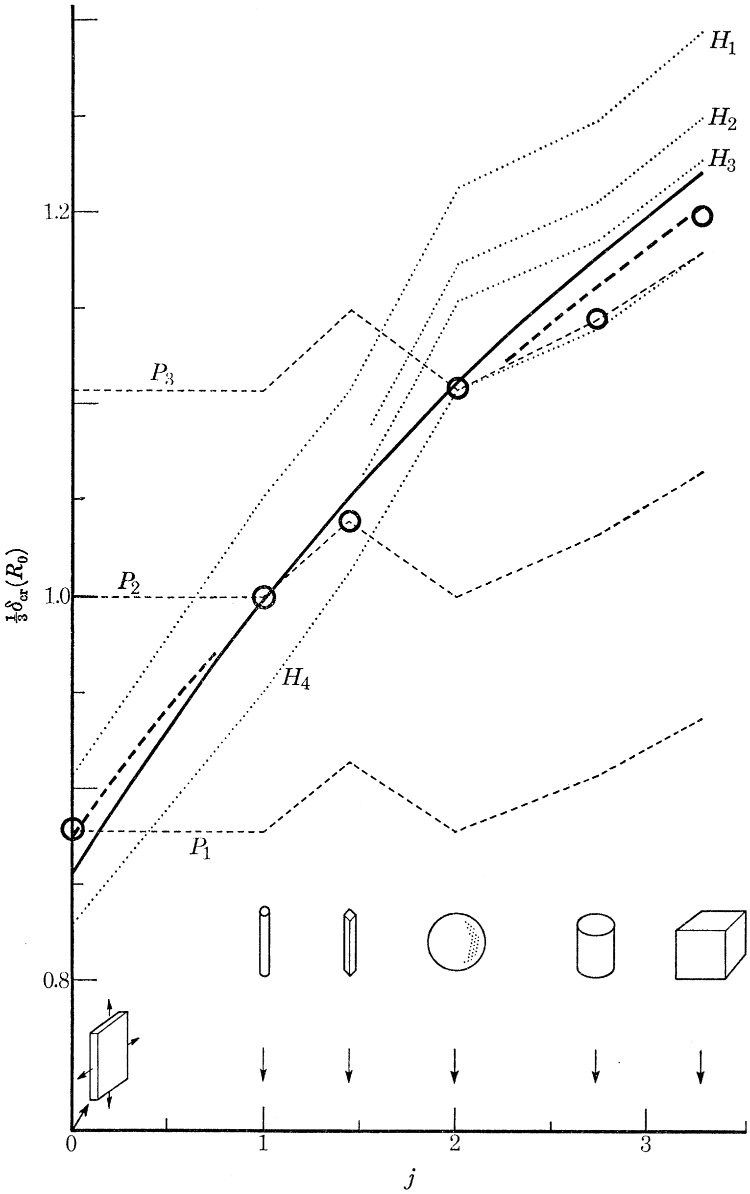

FIGURE 3. Comparison of criticality criteria for various geometries under Frank-Kamenetskii boundary conditions. O, Exact values of $\frac{1}{3}\delta_{\mathrm{cr}}(R_0)$ known for the geometries indicated schematically at the bottom; ——, present result, $F(j)$ (equation 4.10); - - - -, the empirical correlation $(2j+7)/(j+8)$. The labelled broken lines serve to connect the isolated data points generated by earlier approaches. P_1, P_2, P_3 correspond to Wake & Walker's Poisson equivalent slab, cylinder and sphere methods, respectively (equation 7.14). H denotes a criterion based on the Helmholtz length, $\lambda_1^{-\frac{1}{2}}$ (equation 6.2): H_1 represents Khudyaev's upper bound or the generalized Bowes and Thomas estimate (6.4); H_2, H_3, H_4 represent the estimates generated by the quasistationary approach (§7 (b)) when adjusted to give correct results for the ∞ slab, ∞ cylinder and sphere respectively (equation 7.12).

TABLE 3. COMPARISON OF $F(j)$ FROM (4.11) AND EXACTLY KNOWN† VALUES FOR CERTAIN GEOMETRIES

geometry	j	$F(j)$	$F_{ex}(j)$†	$[F(j)-F_{ex}(j)]/F_{ex}(j)$ (%)
∞ slab	0	0.857	0.878	−2.4
∞ circular cylinder	1	1	1	0
∞ square rod	1.444	1.051	1.039	+1.2
sphere	2	1.111	1.107	+0.3
equicylinder‡	2.729	1.177	1.145 ± 0.01	+2.8
cube‡	3.275	1.221	1.198 ± 0.01	+1.9

† $F_{ex}(j) \equiv \frac{1}{3}\delta_{cr}(R_0)$
‡ Corrected result from Parks's calculation (1961).

In order to consider the combined error resulting first from the use of our postulated approximate general solution (3.22) and secondly from the adoption of the simplifying approximation (4.4), we compare the factor $F(j)$ given by (4.11) and the quantity $F_{ex}(j)$ which must be used in (4.10) in order to give the precise results calculated numerically for certain shapes. (Because of the dearth of precise results we have solved the basic equations (3.4), (3.5) numerically for the conveniently simple case of the infinite rod of square cross-section.) Table 3 compares $F(j)$ and $F_{ex}(j)$ for a rather wide range of geometries and figure 3 illustrates the comparison graphically. It is seen that the error incurred in using $F(j)$ to calculate critical conditions is small. Denoting $(F-F_{ex})/F_{ex}$ by $(\Delta F/F)$ and assuming this quantity to be small we find the following errors in other critical quantities:

$$(\Delta\delta/\delta)_{cr} = (\Delta\gamma/\gamma)_{cr} = \Delta F/F \sim 1\,\%,$$
$$(\Delta R_0/R_0)_{cr} = \tfrac{1}{2}\Delta F/F \sim \tfrac{1}{2}\,\%,$$
$$\Delta T_{a,\,cr} = (\boldsymbol{R}T^2_{a,\,cr}/E)\,(\Delta F/F) \sim 0.1\,\mathrm{K},$$

where the numerical values correspond to a 1 % error in F, the observed order of magnitude. We see that our approximate solution may be considered sufficiently precise for practical application, especially in view of other uncertainties discussed in appendix 3.

In order to use our general critical conditions for a particular body it is necessary that R_S and R_0 be evaluated. The former, which equals $3V/S$, presents no difficulty, since V and S may be found from mensuration tables or by straightforward quadrature (see appendix 2(*a*)). For a wide range of interesting geometries evaluation of the mean radius R_0 is simple, though often extremely tedious. For convenience we give in appendix 2(*b*) useful formulae for its evaluation for some rather general shapes (e.g. bodies of rotation, polyhedra, and right cylinders of arbitrary cross-section), and for the evaluation of the contribution to R_0^{-2} of spherical, cylindrical and planar surfaces. This appendix also sets out simple formulae for R_0 for a wide range of particular cases. An examination of these formulae shows that in essence R_0^{-2} has the nature of the mean value of the half-widths in three orthogonal directions, each raised to the power −2. Thus, for the ellipsoid with semi-axes a, b, c, we have

$$\frac{1}{R_0^2} = \frac{1}{3}\left[\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}\right].$$

4(*b*). *The radius of the equivalent sphere under Frank-Kamenetskii boundary conditions*

We base our evaluation of equivalent sphere radii on the relation

$$\delta_{cr}(R_0) = (\gamma R_0^2)_{cr} = 3F(j), \tag{4.10}$$

where
$$F = \frac{2j+6}{j+7} = \frac{2}{3}\left(\frac{3\chi+2}{\chi+2}\right) \tag{4.13}$$
and
$$\chi = \tfrac{1}{3}(j+1) = R_0^2 R_S^{-2}. \tag{4.14}$$
In particular we have for the case of the sphere
$$[\gamma_{cr} R_0^2]_{sph} = [\gamma_{cr} a_0^2]_{sph} = 3F(2) = \tfrac{10}{3}. \tag{4.15}$$
Now $a_{0,sph}$ will be the radius R_{FK} of the equivalent sphere for $Bi = \infty$ when, by definition, the body and the sphere have a common composition and critical explosion temperature, i.e. a common value of γ_{cr}. Hence, equating γ_{sph} given by (4.15) and γ given by (4.10), we find that R_{FK} is given by
$$\frac{R_{FK}^2}{R_0^2} = \frac{5}{3}\left(\frac{\chi+2}{3\chi+2}\right) = \frac{10}{9}\left(\frac{j+7}{2j+6}\right) = \frac{10}{9F}, \tag{4.16}$$
or
$$R_{FK} = (10/9F)^{\frac{1}{2}} R_0. \tag{4.17}$$
Hence the mean radius R_0 is, in a good first approximation, the radius of the equivalent sphere when $Bi = \infty$, the error entailed being especially small for compact bodies ($\chi \simeq 1, j \simeq 2$) since
$$(10/9F)^{\frac{1}{2}} = 1 - \tfrac{2}{45}(j-2) + O([j-2]^2)$$
$$= 1 - \tfrac{2}{15}(\chi-1) + O([\chi-1]^2).$$
For convex bodies we have $\quad 0.930 \leqslant (10/9F)^{\frac{1}{2}} \leqslant 1.138,$

where the least value corresponds to the regular tetrahedron and the greatest to the infinite slab. Thus the (inverse square) mean radius constitutes a readily calculated rough estimate of the Frank-Kamenetskii equivalent sphere radius. It leads to errors in $T_{a,cr}$ for convex bodies not greater than *ca.* $\boldsymbol{R}T_a^2/4E$ (typically less than 5 K). When greater precision is demanded the exact result (4.17) may be used (once R_S has been evaluated).

4 (*b*) (i). *Comparison with Semenov equivalent sphere radii*

A convenient parameter with which to gauge the dependence of equivalent sphere radii on the Biot number is the square of the ratio of the radii under the two extreme conditions, $Bi = 0$ and $Bi = \infty$:
$$\Phi \equiv (R_{FK}/R_S)^2 = (R_{FK}/R_0)^2\,(R_0^2 R_S^{-2}).$$
Using (4.14) and (4.16) we may write
$$\Phi = \left(\frac{R_{FK}}{R_S}\right)^2 = \frac{5}{3}\left(\frac{\chi+2}{3\chi+2}\right)\chi = \frac{5}{27}\left(\frac{(j+1)(j+7)}{j+3}\right), \tag{4.18}$$
or
$$\Phi - 1 = \tfrac{11}{45}(j-2)\,[1+\tfrac{5}{33}(j-2)]\,[1+\tfrac{1}{5}(j-2)]^{-1}$$
$$= \tfrac{11}{45}(j-2)\,[1-\tfrac{8}{165}(j-2)+O([j-2]^2)]. \tag{4.19}$$
We conclude that the equivalent sphere radii differ under the two extreme physical conditions (unless $j = 2$). The departure of Φ from unity is not large for convex bodies: Φ takes its least value $\frac{35}{81} = 0.432$ for the infinite slab and its greatest value 1.494 for the regular tetrahedron. R_{FK} exceeds R_S for compact but angular bodies (e.g. the cube) but is less than R_S for bodies having one principal dimension greatly different to the other two (e.g. thin disks and long rods). The values of Φ and of other shape dependent parameters for some important geometries are set out in table 4.

Table 4. Some important shape-dependent dimensionless parameters for certain simple geometries

parameter	χ	j	lR_S^{-1}	$l^2R_0^{-2}$	$F(j)$	Φ	$\theta_{0,\mathrm{cr}}$
definition	(3.19)	(3.19)	(2.1)	(3.19)	(4.11)	(4.18)	(4.8)
geometry							
∞ slab, $l = \frac{1}{2}$ thickness	0.3333	0	0.3333	0.3333	0.857	0.432	1.187
thin circular disk, $\frac{1}{2}$ thickness l, radius $10l$	0.4790	0.4370	0.4000	0.3340	0.9243	0.5758	1.241
∞ cylinder, l = radius	0.6667	1	0.6667	0.6667	1.0000	0.7411	1.386
long circular cylinder, length $10l$, radius l	0.8061	1.418	0.7333	0.6671	1.050	0.853	1.489
infinite square rod, side = $2l$	0.814	1.443	0.6667	0.5455	1.051	0.860	1.492
sphere, l = radius	1.0000	2	1.0000	1.0000	1.111	1.000	1.622
equicylinder, l = radius = $\frac{1}{2}$ ht.	1.243	2.728	1.0000	0.8047	1.178	1.173	1.778
cube, side = $2l$	1.427	3.280	1.0000	0.7009	1.222	1.298	1.888
regular tetrahedron, side = $2l$	1.729	4.187	2.449	3.4702	1.284	1.494	2.058

5. Criticality when the surface heat transfer coefficient is arbitrary

The results of §§ 3 and 4 constitute a fairly precise general solution of the criticality problem for arbitrary shapes in the Frank-Kamenetskii limit ($Bi \to \infty$), and thus complement the well-known general solution of the problem for the Semenov limit ($Bi \to 0$). There remains the markedly more difficult task of solving the general problem (3.1), (3.2) when the Biot number is arbitrary. This is of the utmost practical importance since frequently the situation is such that neither of the two extremes already discussed can constitute a good description of the actual boundary conditions. The treatment in § 3 of the Frank-Kamenetskii limit depended for its success upon our ability to write down an approximate general solution of the heat balance equation *satisfying the boundary conditions*, and thus upon the very simple form of the condition $\theta = 0$ on S. In the general case we require to solve (3.4) subject to

$$\mathrm{d}\theta/\mathrm{d}n + h\theta = 0 \quad \text{on } S, \quad h = H/\kappa,$$

or

$$\mathrm{d}\theta/\mathrm{d}\rho + hl(\Theta, \phi) = 0 \quad \text{at} \quad \rho = 1$$

(see figure 1), and we see that this boundary condition cannot be satisfied by $\theta = \theta(\rho)$, i.e. that the above approach cannot be extended to the case of arbitrary Bi.

Below we adopt an empirical approach to the solution of the general problem.

5 (a). *Variation of $\delta_{\mathrm{cr}}(R_0)$ with Biot number*

When the Biot number is arbitrary we see that the criticality problem becomes extremely intractable. In the absence of a more precise treatment we give below an empirical formula from which general critical conditions may be calculated and, in partial justification, demonstrate that a diversity of its particular forms give the same results as those derived above and elsewhere. Let us consider the suitability of the equation

$$\frac{1}{\delta_{\mathrm{cr}}(R_0)} = \frac{1}{3F(j)} + \frac{\mathrm{e}}{j+1}\frac{1}{Bi} \tag{5.1}$$

as a repesentation of the condition for criticality for bodies of arbitrary shape and arbitrary *Bi*:

(i) *The Frank-Kamenetskii limit.* As $(Bi)^{-1} \to 0$ equation (5.1) generates the relation $\delta_{cr}(R_0) = 3F(j)$ derived above for a body of arbitrary shape and shown to be correct to within a few parts per cent.

(ii) *The Semenov limit.* As $Bi \to 0$ equation (5.1) generates the relation

$$\frac{e\,\delta_{cr}(R_0)}{(j+1)\,Bi} = \frac{e\,\kappa\gamma_{cr}V}{HS} = e\left[\frac{q\sigma AEV}{HSRT_a^2}\exp\left(-E/RT_a\right)\right]_{cr} = e\,\psi_{cr} = 1,$$

i.e. reduces to Semenov's classical result for arbitrary shape (see § 2) on using the definitions of R_0, j and *Bi*. To the extent that the Frank-Kamenetskii exponential approximation is acceptable this is an *exact* result.

(iii) *Class A geometries, intermediate Biot numbers.* For the infinite slab, infinite cylinder and sphere the geometric relations

$$R_0^2 = 3a_0^2/(j+1), \quad R_S = 3a_0/(j+1)$$

hold, so that (5.1) may be written

$$\frac{1}{\delta_{cr}(a_0)} = \frac{1}{(j+1)\,F(j)} + \left(\frac{e}{j+1}\right)\left(\frac{Ha_0}{\kappa}\right)^{-1}.$$

This result is the same as that derived previously by Thomas (1960) and by Barzykin & Merzhanov (1958) for *all* Biot numbers, except that it involves the approximate expression

$$(j+1)\,F(j) = 0.857, 2, 3.33$$

for the exact values $\delta_{cr}(a_0) = 0.878, 2, 3.32$. With this reservation we may say that (5.1) includes these earlier results for the simple geometries of class A.

It is thus seen that (5.1) gives accurate critical conditions both for all geometries at extremes of the Biot number, and at all Biot numbers for the disparate geometries: slab, cylinder and sphere. We shall further show (in § 6) that (5.1) gives results lying within rigorously derived upper and lower bounds.

5 (*b*). *Equivalent sphere radii for arbitrary Biot number*

The forms of the equivalent sphere radii at high and low Biot numbers have already been considered (see §§ 2 and 4 (*b*)). In this section we consider the form of R_{eq} at intermediate Biot numbers, basing our treatment on the empirical relation (5.1) which, in virtue of the high precision of a great diversity of its particular forms, we conjecture is a good approximation universally.

The concept of equivalence remains vague until a precise specification is given of the conditions under which different bodies are to be compared. The choice will depend on the problem under consideration. We consider that a comparison at constant heat transfer coefficient *H* is generally appropriate.† Accordingly for our present purposes we define the equivalent sphere generally as follows:

> A sphere and a given body are equivalent if, having a common composition and a common surface heat transfer coefficient *H*, they have a common critical ambient temperature. The sphere radius $R_{eq}(H)$ is then the equivalent sphere radius of the given body at that value of the heat transfer coefficient.

† In particular we wish to imply that comparison at constant $Bi = hR_S$ is not usually appropriate.

$R_{eq}(H)$ is to be found from the critical condition (5.1). Thus in general we have

$$\frac{3}{\gamma_{cr} R_0^2} = \frac{1}{F} + \frac{e}{Bi\chi} \tag{5.2}$$

and for a sphere ($\chi = 1$) in particular:

$$\frac{3}{[\gamma_{cr} a_0^2]_{sph}} = \frac{1}{F_{sph}} + \frac{e}{Bi_{sph}}. \tag{5.3}$$

If the sphere and the arbitrary body are to be equivalent we must have

$$T_{a,\,cr} = T_{a,\,cr}(\text{sphere}), \quad \text{i.e.} \quad \gamma_{cr} = \gamma_{cr,\,sph}, \tag{5.4}$$

and
$$H = H_{sph}, \quad \text{i.e.} \quad \frac{Bi_{sph}}{Bi} = \frac{R_S(\text{sphere})}{R_S} = \frac{R_{eq}}{R_S}. \tag{5.5}$$

Combining (5.2) to (5.5), we find

$$\frac{R_0^2}{R_{eq}^2} = \left\{\frac{1}{F_{sph}} + \frac{e}{Bi}\left(\frac{R_S}{R_{eq}}\right)\right\} \Big/ \left\{\frac{1}{F} + \frac{e}{Bi\chi}\right\}, \tag{5.6}$$

and, from the definitions of Φ and χ,

$$\frac{R_S^2}{R_{eq}^2} = \left\{\left(\frac{e}{Bi}\right)\left(\frac{R_S}{R_{eq}}\right) + \tfrac{9}{10}\right\} \Big/ \left\{\left(\frac{e}{Bi}\right) + \tfrac{9}{10}\Phi\right\}. \tag{5.7}$$

This is the basic equation relating R_{eq} to the physical size (through R_S), to the surface heat transfer conditions (through Bi), and to the shape (through $\Phi(j)$) of the given body. It may be conveniently expressed in the dimensionless form

$$\beta(\Phi - P^2) = P - 1, \tag{5.8}$$

where $P = R_{eq}/R_S$ is a useful reduced measure of R_{eq} and β is a revised Biot number

$$\beta = 9Bi/10e = \left(\frac{27}{10e}\right)\left(\frac{HV}{\kappa S}\right). \tag{5.9}$$

On solving (5.8) for P we find

$$P = R_{eq}/R_S = [\surd\{1 + 4\beta(1 + \beta\Phi)\} - 1]/2\beta, \tag{5.10}$$

so that when the Biot number is small ($\beta \ll 1$)

$$P = 1 + [\Phi - 1]\,\beta - [2(\Phi - 1)]\,\beta^2 + O(\beta^3), \tag{5.11}$$

and when the Biot number is large

$$P = \surd\Phi\{1 - [\surd\Phi - 1]/2\beta\Phi + O(\beta^{-2})\}. \tag{5.12}$$

We illustrate the form (5.10) of $P(\beta, \Phi)$ in figure 4. It is seen that P varies monotonically from unity at $\beta = 0$ to $\surd\Phi$ at $\beta = \infty$, i.e. that as the heat transfer coefficient H is varied from very low to very high values the equivalent sphere radius R_{eq} varies monotonically from R_S to R_{FK}. The ratio R_{eq}/R_S may increase or decrease with Biot number depending on the shape of the body. If the shape factor j is 2 then R_{eq} always has the value R_S.† Although P may decrease as β is increased (if $\Phi < 1$, $j < 2$) it is readily shown from (5.10) that the quantity $[\partial R_{eq}/\partial R_S]_{j,\,h}$ is

† It should be noted, however, that the constancy of $P(\beta)$ for the sphere itself is merely the trivial consequence of adopting the sphere as the reference shape.

positive for all shapes j, that is (as we should expect physically), that no matter what the geometry the equivalent sphere radius increases with the physical size (R_S), under conditions of constant heat transfer coefficient.

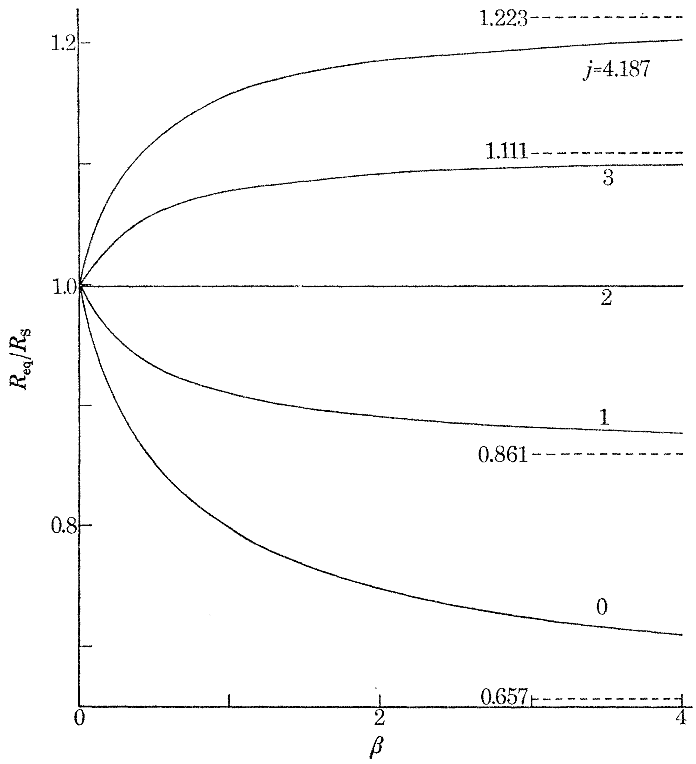

FIGURE 4. Dependence of the reduced equivalent sphere radius $P = R_{eq}/R_S$ upon modified Biot number β, according to (5.10). - - - - -, Value attained in the Frank-Kamenetskii limit, $\beta \to \infty$. The curves shown correspond to the entire range of convex geometries. Slab, $j = 0$; cylinder, $j = 1$; sphere, $j = 2$; regular tetrahedron, $j = 4.187$.

6. Rigorous bounds on critical parameters

Our derivation of the critical conditions in the Frank-Kamenetskii limit (and for intermediate values of the Biot number) demands justification *a posteriori*. This is supplied (table 5 and figure 3) by a comparison with known exact results, but their paucity precludes a more exhaustive test. We receive additional confidence in our results for the critical values of γ from the fact that they lie within rather close rigorous bounds that we are able to derive, both for arbitrary Biot number and for a considerably larger set of geometries than that for which exact numerical results are available. Our derivation of upper and lower bounds is founded on the important but apparently little known results of Khudyaev (1963, 1964).

6 (*a*). *Upper bound on* γ_{cr}

Khudyaev compares the exact solution of the Poisson–Boltzmann equation

$$\operatorname{div} \mathbf{grad}\, \theta + \gamma\, e^{\theta} = 0 \quad \text{in } V, \tag{6.1}$$

with the solution θ_1, corresponding to the least eigenvalue λ_1, of the *associated Helmholtz equation*

$$\operatorname{div} \mathbf{grad}\, \theta + \lambda\theta = 0 \quad \text{in } V, \tag{6.2}$$

TABLE 5. COMPARISON OF UPPER AND LOWER BOUNDS ON THE CRITICAL VALUE OF $\delta(a_0)$ AT INFINITE BIOT NUMBER (FRANK-KAMENETSKII BOUNDARY CONDITIONS) FOR THOSE GEOMETRIES FOR WHICH EXACT RESULTS ARE AVAILABLE

geometry	j (3.19)	δ_l/δ_{cr} (6.9)	$\delta_{cr}(a_0)$†	δ_u/δ_{cr} (6.4)	δ/δ_{cr} (4.10)
∞ slab, $a_0 = \frac{1}{2}$ width	0	0.835	0.878	1.033	0.975
∞ cylinder, a_0 = radius	1	0.735	2	1.052	1
∞ square rod, side = $2a_0$	1.444	0.732	1.70	1.067	1.01
sphere, a_0 = radius	2	0.662	3.32	1.095	1.003
equicylinder, radius = a_0	2.728	0.660	2.76	1.087	1.03
cube, side = $2a_0$	3.280	0.651	2.52	1.079	1.019

† The column $\delta_{cr}(a_0)$ shows results derived exactly or from numerical solutions.

the boundary condition being in both cases (and always below)

$$\mathrm{d}\theta/\mathrm{d}n + h\theta = 0 \quad \text{on } S, \tag{6.3}$$

and is able to demonstrate that no solution θ of (6.1) can exist if $\gamma > \mathrm{e}^{-1}\lambda_1$, i.e. that

$$\gamma_{cr} \leqslant \gamma_u = \mathrm{e}^{-1}\lambda_1 \tag{6.4}$$

gives an upper bound on the critical value of γ.† The associated Helmholtz equation (6.2) is separable for certain geometries (these are tabulated in full by Morse & Feshbach (1953)), so that, for these, precise expressions for λ_1 can be found—although even with the simplifying restriction $hR_S \equiv Bi \to \infty$ the calculation is rarely simple. For the geometries which we have examined (class A, finite circular cylinder, rectangular brick) the precise results (where available) and the present results (equation (5.1)) lie less than 10% below the upper bound $\gamma_u = \mathrm{e}^{-1}\lambda_1$ when $Bi \to \infty$, and approach the upper bound as $Bi \to 0$ (the Semenov limit). The two extreme forms for the rectangular brick ($2a \times 2b \times 2c$) illustrate well the general form of the results for γ_u:

$$\gamma_u = \mathrm{e}^{-1}\lambda_1(Bi \to \infty) = \frac{\pi^2}{4\mathrm{e}}\left[\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}\right]; \quad \frac{\pi^2}{4\mathrm{e}} = 0.907, \tag{6.5}$$

$$\gamma_u = \mathrm{e}^{-1}\lambda_1(Bi \to 0) = \mathrm{e}^{-1}h\left[\frac{1}{a}+\frac{1}{b}+\frac{1}{c}\right] = \frac{HS}{\kappa V\mathrm{e}}. \tag{6.6}$$

Equation (6.6) can be rearranged to give

$$\mathrm{e}\,\psi_u = 1, \tag{6.7}$$

which shows that ψ_u tends to the exact value ψ_{cr} in the Semenov limit. (It can indeed be shown that this result is true generally). In the limit of large Bi (6.5) gives, for the cube of side $2a_0$, the result

$$\delta_{cr}(a_0) \leqslant \delta_u(a_0) = 3\pi^2/4\mathrm{e} = 2.72,$$

whereas the computed value (Parks 1961) is 2.516 ± 0.01 and the present approach would give the value 2.56.

6(*b*). *Lower bound on* γ_{cr}

A lower bound on γ_{cr} can be established by making use of Khudyaev's sufficient condition (Khudyaev 1964) for the existence of a solution of (6.1), subject to the general boundary condition (6.3). By considering the *associated Poisson equation*

$$\left.\begin{aligned} \operatorname{div}\mathbf{grad}\,\Gamma + 1 &= 0 \quad \text{in } V, \\ \mathrm{d}\Gamma/\mathrm{d}n + h\Gamma &= 0 \quad \text{on } S, \end{aligned}\right\} \tag{6.8}$$

† Allied results have been derived subsequently by Keller & Cohen (1967), Fujita (1969) and Joseph & Sparrow (1970).

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we can demonstrate that a solution of (6.1) exists if $e\gamma \mathit{\Gamma}_m \leqslant 1$, i.e. that

$$\gamma_{cr} > \gamma_l \equiv e^{-1}\mathit{\Gamma}_m^{-1}, \tag{6.9}$$

where $\mathit{\Gamma}_m$ is the greatest value of $\mathit{\Gamma}$ achieved in (6.8). The associated Poisson equation is soluble analytically when the Green function for the region V is known (Carslaw & Jaeger 1959), and the corresponding $\mathit{\Gamma}_m$ is then readily found. It can be shown that in the limit $Bi = hR_S \to 0$ the lower bound γ_l given by (6.9) approaches the exact value of γ_{cr}. When Bi is large γ_l and γ_{cr} are substantially different (see table 5). Thus for compact bodies (sphere, cube, equicylinder) we have $\gamma_l \simeq 2\gamma_{cr}/3$, the discrepancy $(\gamma_{cr}-\gamma_l)$ being less for the infinite slab and cylinder. Unfortunately $\mathit{\Gamma}_m$ can only be found analytically for rather simple shapes and, in general, $\mathit{\Gamma}_m$ is not expressed as a simple function of the characteristic dimensions, but rather as an infinite series. Expressions for our lower bound are thus available at present only for a restricted range of geometries. In addition to the geometries set out in table 5 we have examined† the case of the finite cylinder at infinite Bi. The present critical results all lie some 30 to 60 % above γ_l.

By considering our upper and lower bounds together we know that γ_{cr} is constrained to lie within a strip of which the width $\gamma_u - \gamma_l$ is *ca.* 40 % of the greatest value γ_u when Bi is large; becoming zero when Bi is zero. The fact that the present results for the diverse geometries cited lie within this strip suggests that they will never be seriously in error for more general geometries.

Since Khudyaev's upper bound $\gamma_u = e^{-1}\lambda_1$ is usually less than a 10 % over estimate of γ_{cr}, it could itself be used as a rough estimate for γ_{cr}, but in general its evaluation is impossible analytically. However, the labour in applying the present critical results to a particular geometry is quite trivial by comparison with that involved in finding either γ_u or γ_l (even when an analytical approach is possible).

Comparison with the sphere of the same volume

Gray & Lee (1967*b*) have suggested and Wake (1971) has demonstrated rigorously that under Frank-Kamenetskii boundary conditions no body has a lower critical ambient temperature than that of the sphere of the same volume. Thus $3.32\,(4\pi/3V)^{\frac{2}{3}}$ is a lower bound on γ_{cr}. This bound is superior to (6.9) for physically compact bodies (Boddington, Gray & Harvey 1971), but when the shape factor j is less than *ca.* 1.7 it becomes unusably low.

7. Status of previous approaches

Although a number of approaches to the problem of steady-state criticality have previously been explored, no account of their validity, precision or interrelation is available. The above discussion permits an appraisal of earlier results. Because these have sometimes been formulated diffusely and restrictively, we take the opportunity below of making them explicit and generalized. The present results are found to be more precise and more convenient to use than the generalized forms of earlier results.

7 (*a*). *Inscription and escription*

Gray & Lee (1967) have sought upper and lower bounds on γ_{cr} for complex geometries by inscribing or escribing the body under consideration with bodies whose γ_{cr} values are known. They thus adopt the tacit conjecture, first explicitly formulated by Gel'fand (1959), that if body (2) completely encloses body (1) then $T_{a,cr}(2) < T_{a,cr}(1)$. This conjecture is not universally valid,

† Results for a few additional geometries can readily be derived from the work of Wake & Walker (1964) (see §7 (*c*)).

since we have shown in § 2 that there are cases for which removal of part of the body *decreases* the critical ambient temperature under Semenov boundary conditions. A general analysis of the conditions under which the conjecture is correct would be very difficult, but we can readily discuss the interesting case of Frank-Kamenetskii boundary conditions.

Let a body S_2 entirely enclose a body S_1 and let the heat balance equation in each be the Poisson–Boltzmann equation (6.1), subject to the boundary condition $\theta = 0$ on S. Further suppose that the common value of γ is $\gamma_{cr}(S_2)$. Then the solution of (6.1) for body (2), θ_2, (which exists by hypothesis) will serve as the upper function $\bar{\theta}_1$ in Khudyaev's existence theorem (1963, 1964) and a solution θ_1 of (6.1) for body (1) exists with $\gamma = \gamma_{cr}(S_2)$. We conclude that

$$\gamma_{cr}(S_1) \geqslant \gamma_{cr}(S_2),$$

and we may write

$$\gamma_u(S_1) \geqslant \gamma_{cr}(S_1) \geqslant \gamma_{cr}(S_2) \geqslant \gamma_l(S_2), \tag{7.1}$$

so long as S_1 is in V_2 and the two bodies are subject to Frank-Kamenetskii's boundary condition ($\theta_S = 0$, $Bi \to \infty$). Thus Gray & Lee's concealed conjecture is valid for $Bi \to \infty$ (the conditions under which they applied it) but probably not under other conditions (since the proof given above breaks down for arbitrary Bi and we have counter-examples at $Bi = 0$). Inequalities (7.1) may be used when $Bi \to \infty$ without restriction on the shapes of S_1 and S_2, and in particular when one or both have concavities or even internal cavities (so long as $\theta = 0$ on the internal surfaces). The inequalities also show how known bounds may be transferred from one body to another, and thus supplement our earlier discussion (§ 6) of upper and lower bounds.

The physical significance of (7.1) is that removal of material from a body of exothermic reactant always increases its critical ambient temperature $T_{a, cr}$ if *all* the old and new surfaces are held at some ambient temperature, T_a. The reservation is crucial, since it is readily envisaged that, by creating non-conducting cavities just below the surface of a body, the principal mass is effectively insulated from its outer surface and $T_{a, cr}$ may be *lowered.*

As applied by Gray & Lee equation (7.1) did not generate very close upper and lower bounds because only bodies for which an exact value of γ_{cr} was to hand were used as interior and exterior bodies, and these could not give a 'close fit' to the geometry under study. If, however, use is made of the γ_{cr} values generated by our present results (4.10) for a diversity of geometries then (with their precision) we can estimate close upper and lower bounds for geometries not tabulated in appendix 2. Clearly such a procedure must be *ad hoc.*

7 (*b*). *Frank-Kamenetskii's quasistationary equivalence*

Frank-Kamenetskii (1955) has postulated plausibly that the effective size of a body may be gauged from the relaxation time of the exponential decay of the internal temperature profile in the quasistationary state (i.e at very large times) and has used this technique to derive an expression for the criticality of finite circular cylinders ($Bi \to \infty$, only), normalizing his result by choosing a proportionality constant which ensures the known exact result for the infinite cylinder. Wake & Walker (1964) have independently suggested an identical approach for (and have applied it to) some further geometries, again only for Frank-Kamenetskii boundary conditions.† Thomas (1958) has extended this technique for the class A geometries to the case of arbitrary Biot number and Bowes (1970) has applied it to the rectangular brick, but their

† This approach should not be confused with a second approach given in the same paper (and discussed in §7 (*c*)).

approach is superior in that the proportionality constant is calculated rather than enforced.† Thomas & Bowes's approach can be generalized directly to arbitrary geometry and Biot number and can thus be compared generally with the present approach and others.

We consider the inert decay of an initial temperature profile, $\theta = \theta(t=0)$ in V, subject to the usual boundary condition (6.3). This is governed by the equation

$$\frac{\partial \theta}{\partial t} = \left(\frac{\kappa}{\sigma c}\right) \operatorname{div} \mathbf{grad}\, \theta, \tag{7.2}$$

the solution of which is readily shown to be

$$\theta = \sum_{i=1}^{\infty} A_i \theta_i \, e^{-\lambda_i D t}, \tag{7.3}$$

where t is the time, $D \equiv \kappa/\sigma c$, the θ_i and λ_i are the normalized eigenfunctions and eigenvalues of the associated Helmholtz equation (6.2), and A_i are constant amplitudes for given initial conditions:

$$A_i = \int_V \theta_i \theta(t=0)\, dV. \tag{7.4}$$

The eigenvalues λ_i satisfy (Mikhlin 1964)

$$0 < \lambda_1 < \lambda_2 \leqslant \lambda_3 \leqslant \lambda_4 \ldots,$$

so that at long times the temperature anywhere in the body obeys

$$\partial\theta/\partial t = -\lambda_1 D \theta; \quad \text{in } V, t \to \infty, \text{ inert.} \tag{7.5}$$

Since (7.5) is true everywhere, a similar result is valid for the mean temperature

$$\overline{\theta} = \frac{1}{V}\int \theta \, dV:$$

$$d\overline{\theta}/dt = -\lambda_1 D \overline{\theta}; \quad t \to \infty, \text{ inert,} \tag{7.6}$$

so that the mean heat loss rate is given by

$$-\overline{\operatorname{div} \mathbf{grad}\, \theta} = \lambda_1 \overline{\theta}; \quad t \to \infty, \text{ inert.} \tag{7.7}$$

If we now conjecture, following Thomas (1958), that: (i) equation (7.7) holds not merely in the quasistationary, inert case but also in the steady-state reactive case and (ii) that the mean value over the volume of the quantity e^{θ} may be satisfactorily approximated by $e^{\overline{\theta}}$, then the volume average form of the basic steady-state equation (6.1) becomes

$$\lambda_1 \overline{\theta} = \gamma e^{\overline{\theta}} \quad \text{or} \quad \gamma = \lambda_1 \overline{\theta} e^{-\overline{\theta}}. \tag{7.8}$$

Clearly this result predicts the critical value:

$$\gamma_{cr}(\text{BT}) = e^{-1}\lambda_1 \equiv \gamma_u. \tag{7.9}$$

Thus *the generalized Bowes and Thomas method leads to an estimate of* γ_{cr} *which is precisely the upper bound given by Khudyaev* (1964, see (6.4)). We conclude in particular that for all geometries $\gamma_{cr}(\text{BT})$ is an overestimate of γ_{cr}, but for many geometries is not in error by more than 10 %, and becomes exact in the Semenov limit.

† This apparent logical advantage is however meretricious, since the derivation supposes certain quantities to be equal when they are known only to be similar in magnitude.

The critical conditions derived by Frank-Kamenetskii and by Wake & Walker are slightly different. Again they purport to apply only at infinite Biot number, but are constrained to give the correct critical value for a certain reference geometry. Thus Wake & Walker's method essentially assumes that bodies are equivalent when their Helmholtz lengths $\lambda_1^{-\frac{1}{2}}$ are the same, takes the known critical condition *for the reference body* and assumes it to be valid for all geometries:

$$\delta_{cr}(\lambda_1^{-\frac{1}{2}}) = \gamma_{cr}\lambda_1^{-1} = \delta_1^{ref} \equiv \delta_{cr}^{ref}(a_0)\,[a_0^2\lambda_1^{ref}]^{-1}. \tag{7.10}$$

Their method thus gives rise to the critical condition

$$\gamma_{cr}(\mathrm{WW1}) = \lambda_1\delta_1^{ref}, \tag{7.11}$$

or, if a critical value of δ based on some convenient characteristic dimension b_0 is quoted,

$$\delta_{cr}(b_0, \mathrm{WW1}) = \gamma_{cr}(\mathrm{WW1})\,b_0^2 = \left[\frac{b_0^2\lambda_1}{a_0^2\lambda_1^{ref}}\right]\delta_{cr}^{ref}(a_0). \tag{7.12}$$

The results derived from (7.11) and (7.12) depend rather feebly on the geometry adopted for reference. Thus for class A geometries $\delta_1^{ref} = [0.356, 0.350, 0.336]$ for $j = [0, 1, 2]$ and, correspondingly, in the Frank-Kamenetskii limit the generalized results of Wake & Walker and of Bowes and Thomas are related by

$$\gamma_{cr}(\mathrm{WW1})/\gamma_{cr}(\mathrm{BT}) = \mathrm{e}\,\delta_1^{ref} = 0.967, 0.950, 0.914, \text{ for class A reference bodies.}$$

All the above results for criticality based on the Helmholtz lengths $\lambda_1^{-\frac{1}{2}}$ derived from the quasistationary régime (i.e. those of Frank-Kamenetskii, Bowes, Thomas, and Wake & Walker) suffer from two deficiencies at large Biot numbers. First no single proportionality constant will generate γ_{cr} with errors less than 5 % over the entire range of convex geometries (see figure 3), and secondly values of λ_1 are available only for a limited range of geometries.

7 (*c*). *Wake & Walker's equivalence: the Poisson length*

An alternative method for gauging an effective size of a body, and one which seems more plausible than the quasistationary approach, is also due to Wake & Walker (1964). Bodies are defined to be equivalent when their sizes are such that, when subjected to the same constant (but arbitrary) internal heat evolution rate, the greatest temperatures achieved in the steady state are the same. This equivalence may be described more generally as follows. For each body the associated Poisson equation (6.8) is solved and the greatest value Γ_m is found. The bodies are equivalent when their *Poisson lengths* $\Gamma_m^{\frac{1}{2}}$ are equal, i.e. when $\Gamma_m = \Gamma_m^{ref}$. We thus have

$$a_0^2(\mathrm{eq}) = [\Gamma_m^{ref}a_0^{-2}]^{-1}\,\Gamma_m, \tag{7.13}$$

where a_0 is the characteristic dimension of the reference body the equivalent value of which is sought, and the quantity in square brackets is a dimensionless constant for the given reference shape. If we chose the half-width of the class A geometries for reference purposes, the term in square brackets equals $2(j+1)$ and $a_0(\mathrm{eq})$ given by (7.13) is the equivalent half-width (radius) of the body under consideration. Critical conditions may then be expressed in this approximation by

$$\gamma_{cr}\,a_0^2(\mathrm{eq}) = \delta_{cr}^{ref},$$

or

$$\gamma_{cr}(\mathrm{WW2}) = \left\{\frac{\delta_{cr}^{ref}}{2(j+1)}\right\}\Gamma_m^{-1}. \tag{7.14}$$

This result gives critical values of γ which may entail errors of more than 15 % if a range of geometries is compared with a single reference body. The results are fairly accurate however if the reference body is chosen to be geometrically very similar to the body under consideration (see figure 3). Such an *ad hoc* approach is demanded if high precision is to be secured. The major drawback, however, is the limited number of geometries for which values of Γ_m are available. It should be noted that Wake & Walker's results based on a fixed reference body are proportional to our lower bounds γ_1 given by (6.9). Thus for the equivalent sphere method we have

$$\gamma_{cr}(\mathrm{WW2})/\gamma_1 = 3.32\mathrm{e}/6 = 1.51.$$

Although Wake & Walker propose the present scheme of equivalence only for very large $Bi = hR_S$, we may generalize it by defining bodies to be equivalent when their Poisson lengths (7.13) are equal at some fixed value of h. When this is done the evaluation of Γ_m becomes longer (and sometimes impossible analytically) but the values of γ_{cr} generated become more precise as Bi is diminished. In the Semenov limit $h \to 0$ we have

$$\Gamma_m \to V/hS \to \lambda_1^{-1}; \quad \text{all geometries,} \tag{7.15}$$

so that bodies are equivalent when they have the same surface to volume ratio, and the γ_{cr} found from the generalized approach become exact no matter what body is chosen as reference.

8. Discussion

Our major result is the identification of critical conditions for bodies of arbitrary shape and arbitrary surface heat transfer coefficient by means of relatively simple expressions either for the critical value of a universally defined δ (equation (5.1)) or for the ratio of the equivalent sphere radius and the Semenov radius (equation (5.10)). These equations generate with high precision known exact results corresponding to a great diversity of particular cases, and are applicable directly to a body of any shape having a centre of symmetry and such that the entire surface is 'visible' from that centre. In the Frank-Kamenetskii (large Biot number) limit the validity of (5.1), (5.10) has been tested only for convex bodies. We would not assert that these results will be accurate (in this limit) for bodies with important concavities, although they are asymptotically exact in the opposite (Semenov) limit.

Rapid calculations of critical conditions for a wide range of geometries may be made by using (5.1) and (5.10) in conjunction with the information set out in appendix 2 on R_S, R_0 and on certain geometry dependent dimensionless numbers.

It was possible to give a plausible but not a rigorous justification of our derivation (§§ 3 to 5) of the criterion for criticality. Ultimately we justify our derivation on the basis of the precision of its results. We note first that critical values of γ predicted here lie within closely adjacent, shape-sensitive upper and lower bounds (§ 6) and, secondly, that in the Frank-Kamenetskii limit ($Bi \to \infty$, figure 3) our criterion is very precise for many widely disparate geometries. Certainly equations (4.10), (5.1) and (5.10) constitute excellent correlations of all exactly known results.

In practical applications even exact solutions of our basic steady-state equations (3.1) and (3.2) must be used with care, for in real situations we must make proper allowance for the effect of reactant consumption (low exothermicities) and for the discrepancy between the Arrhenius and Frank-Kamenetskii temperature dependences of reaction rate (low activation energies).

These difficulties are an inevitable feature of all steady-state theories. We indicate in appendix 3 how they may be surmounted for arbitrary reactant geometry and arbitrary Biot number.

A deficiency of our present approach is that it does not apply to a body without a centre. On the other hand, the Poisson and Helmholtz lengths are universally defined, so that the other generalized but not very precise methods do apply to such bodies. The corresponding calculations are, however, usually so complex that it might be deemed more appropriate to devote the labour to the exact numerical solution of the Poisson–Boltzmann equation.

In the absence of a superior procedure, we suggest that our results may be applied to bodies lacking a centre, but having an axis of symmetry, in the following way. The mean size R_0 is evaluated everywhere on the axis (using the results of appendix 2) and that point for which R_0 is a maximum is taken as the origin (or point at which the greatest temperature is achieved). The critical conditions are then evaluated precisely as for a body with a centre.

When applied to a hemisphere of radius a_0 this method gives $\delta_{cr}(a_0) = 6.27$, whereas the Khudyaev upper bound (6.4) gives $\delta_u(a_0) = 7.42$, and our experience of this upper bound (see table 5) suggest that it will be *ca.* 9% above the correct critical value, so that we should estimate from it $\delta_{cr}(a_0) \simeq 6.75$. A precision of this order will suffice in certain practical applications.

There remain other more complex geometries (expecially those having more than one bounding surface) to which our approach cannot be extended. Here the best recourse is the Khudyaev upper bound and often the best route to the evaluation of λ_1 is a variational one. For example, we can establish in this way that the critical value of δ_{FK} for the tore (doughnut) (based on the radius of the circular cross-section) is less than $6/e = 2.2$, irrespective of its other characteristic dimensions. Unfortunately the application of even this simple method to bodies of low symmetry, e.g. Krook's geometry (Dickens 1853), is very tedious.

It has been suggested (Gray & Lee 1967*a*, *b*; Wake & Walker 1964) that for $Bi \to \infty$, Wake & Walker's results based on the Poisson length and the quasistationary results are equivalent. It is clear from §§ 6 and 7 and from figure 3 that this is not the case. First there are several quasi-stationary methods and several reference bodies to choose from when using the Poisson method of Wake & Walker. Even when a unique quasistationary and a unique Poisson method are selected for comparison, the $\gamma_{cr}^{-\frac{1}{2}}$ values are proportional in one case to the Helmholtz length $\lambda_1^{-\frac{1}{2}}$ and in the other to the Poisson length $\Gamma_m^{\frac{1}{2}}$. When $Bi \to \infty$ these two quantities exhibit only a very crude proportionality; even for the class A geometries they are not simply related. In the Semenov limit $Bi \to 0$, they do indeed become equal, but there the criticality problem for arbitrary shapes is trivial, since Semenov's original treatment already constitutes a complete solution (Semenov 1928). When the Biot number is non-zero the Poisson length is greater than the Helmholtz length for all geometries. To demonstrate this, Γ and θ_1 given by (6.2), (6.3) and (6.8) are used as the two functions in Green's theorem, giving

$$\int_V [\theta_1 \nabla^2 \Gamma - \Gamma \nabla^2 \theta_1]\,\mathrm{d}V = \int_V \theta_1[\lambda_1 \Gamma - 1]\,\mathrm{d}V = 0.$$

Since θ_1 is non-negative, $[\lambda_1 \Gamma - 1]$ must somewhere become zero, and we may conclude that $\lambda_1 \Gamma_m$ must exceed unity, i.e. that *at any given value of h* and for all bodies V:

$$\text{Poisson length} = \Gamma_m^{\frac{1}{2}} > \lambda_1^{-\frac{1}{2}} = \text{Helmholtz length.}$$

We may understand the reason for the failure of Wake & Walker's method (based on the Poisson length) to give precise results when $Bi \to \infty$ for disparate geometries in the following way. The method considers bodies to be equivalent when the central temperature rises (proportional to Γ_m) are the same in systems with a temperature independent rate. In real systems (with non-zero γ) some error will be incurred because there will be a significant variation of the internal temperature. Equally important, however, is the fact that the temperature excess at criticality depends upon shape through $\theta_{0,\,cr} = 2\ln[\frac{1}{4}(j+7)]$. Bodies which are 'Poisson equivalent' will have different critical ambient temperatures if their shape factors differ. This effect is manifested, for example, in the low accuracy of the Poisson equivalent sphere method when applied to the slab or to infinite cylinders (see figure 3). Thus *in the present approximation* Wake & Walker's equivalent sphere criterion is†

$$\gamma_{cr}(\mathrm{WW2}) = 3.32R_0^{-2},$$

a form which lacks the shape factor $F(j)$ of the superior condition (4.10).

8 (*a*). *Applications*

Our present results have a diversity of applications, a few of which we outline below.

8 (*a*) (i). *The effects of scaling and cladding of reactant masses*

In general the sequence of critical explosion temperatures of a set of explosive bodies of arbitrary (differing) shape *is not conserved* when the set of bodies is subjected either to scaling by a common factor or to an alteration of the common surface heat transfer coefficient (as a result of changes in the thermal environment of the set, for example, changes in the thickness and thermal conductivity of an enclosing shell of inert material). The sequence of $T_{a,\,cr}$ corresponding to two bodies having different shape factors j may become reversed. This consequence follows immediately from (5.10) and indicates that care should be exercised in the application of small-scale modelling to full-scale criticality phenomena.

8 (*a*) (ii). *End corrections for a cylindrical reactant mass*

The finite right circular cylinder is a commonly occurring geometry in both gaseous and solid studies, and it is often supposed that in the Frank-Kamenetskii limit the corresponding critical condition is $\delta(a_0) = 2$ (where a_0 is the radius), if the cylinder is 'long'. If Frank-Kamenetskii's result (1955) is used the correction to $\delta_{cr}(a_0)$ is of the order a_0^2/l_0^2, where the length is $2l_0$. Our result (appendix 2 (*b*) (iii)), however, for small a_0/l_0 is

$$\delta_{cr}(a_0) = 2[1+\tfrac{2}{9}(a_0/l_0)],$$

which shows that even for a cylinder four diameters long the correction to be applied is as large as 6 %. On the other hand, for a cylinder of which the length equals the diameter Frank-Kamenetskii's result gives a value (2.98) for δ_{cr} which is 8 % too large (see table 5).

8 (*a*) (iii). *Calorimetry of subcritical régimes*

Our general solution (3.22), or its simpler approximate form (4.5), constitutes a complete and generally rather precise solution of the problem of relating isothermal heat evolution rates to observed maximum temperature rises in the steady state, in the spirit of Wake & Walker's work (1964) on this problem. In this connexion it may be noted that geometries with high j values (those which are compact but angular) may give central temperature excesses in the steady-state which exceed the critical value for the sphere $\theta_{0,\,cr} = 1.607$. The greatest value for convex geometries is for the regular tetrahedron, $\theta_{0,\,cr} = 2.06$. It emerges from a study of numerical

† Since from (3.22) we have $\Gamma_m \simeq \frac{1}{6}R_0^2$.

solutions that although the central temperature excess θ_0 is given fairly precisely by (4.5) for subcritical situations ($\gamma \ll \gamma_{cr}$, $\Delta\theta_0/\theta_0 \lesssim 5\,\%$) the error in the critical value of θ_0 may be larger (*ca.* 10 %). Essentially this is because θ_0 changes extremely rapidly with γ as criticality is approached, so that small errors in our approximate relations $\gamma(\theta_0)$, $\delta(\theta_0)$ inevitably generate substantial errors in the location of the θ_0 for which $\mathrm{d}\theta_0/\mathrm{d}\delta = \infty$.

8 (*a*) (iv). *Effective heat transfer coefficient in time-dependent régimes*

To give a description of time-dependent régimes often requires a treatment in terms of an average temperature, for the problem is otherwise extremely intractable. Thomas (1960) and Barzykin, Gontkovskaya, Merzhanov & Khudyaev (1964) have shown how this may be done for class A geometries. We may generalize the method on the basis of equation (5.1) by writing

$$H_{\text{eff}}^{-1} = H^{-1} + \frac{j+1}{3\mathrm{e}F(j)}\frac{R_{\mathrm{S}}}{\kappa}.$$

This relation defines the effective quantity H_{eff} which may be used in an averaged description of the problem, in which the temperature is taken to be uniform and in which the heat loss is calculated as $H_{\text{eff}}S(T-T_{\mathrm{a}})$. It is so defined that the equation describing the time dependent régime under Semenov boundary conditions

$$\frac{\partial\bar{\theta}}{\partial\tau} = -\bar{\theta} + \psi\,\mathrm{e}^{\bar{\theta}}, \quad \tau = \frac{HSt}{V\sigma c},$$

may be applied to the *mean* temperature excess when Bi is arbitrary *and always lead to the correct critical conditions* (5.1), so long as H in the definitions of τ and ψ is replaced by H_{eff}. This technique enables us to estimate times to explosion for bodies of arbitrary shape following the methods for example of Gray & Harper (1959) or of Karim (1970).

8 (*a*) (v). *Régimes in which heat evolution is temperature-independent*

Although no critical phenomena are associated with such régimes a knowledge of the corresponding temperature distribution within complex geometries is of interest in certain practical situations, e.g. where the uniform heat evolution rate is due to electrical heating (usually in effectively infinite cylinders of arbitrary cross-section) or to nuclear fission. The exact description is, of course, furnished by the solution of the Poisson equation, but an excellent approximation is to hand for the Dirichlet (Frank-Kamenetskii) problem when, as is frequently the case, the solution for the region under consideration is not available. Thus the limiting form for the temperature distribution (3.22) as y tends to zero ($\mathrm{e}^{\theta} \to 1$, everywhere) is

$$\theta = \theta_0(1-\rho^2); \quad \theta_0/\gamma = \Gamma_{\mathrm{m}} = \tfrac{1}{6}R_0^2,$$

where θ/θ_0 is to be interpreted as $(T-T_{\mathrm{a}})/(T_0-T_{\mathrm{a}})$, and θ_0/γ as $\kappa(T_0-T_{\mathrm{a}})/Q$; Q being the heat evolution rate per unit volume. This approximate temperature distribution yields maximum temperature excesses not more than 5 % in error for convex geometries, and may remain reasonably accurate for star-shaped geometries. In conjunction with our tabulated expressions for the mean size R_0, it may be applied with facility to a wide range of geometries.

8 (*b*). *Conclusions*

Of the several methods available for estimating the critical sizes of convex bodies with a centre, the present one (i) has the best accuracy everywhere over a full range of shapes, (ii) is unique in its universal applicability, and (iii) is unique in requiring no more than quadrature (for the evaluation of V, S and R_0) for application to any geometry and any Biot number.

Were it deemed necessary, the precision of our present results in the Frank-Kamenetskii limit could be improved for $j < 1$ by using the exact critical condition (4.3) instead of the approximation (4.7). Our $F(j)$ values would then be exact for both the infinite slab and the infinite circular cylinder. It can also be seen from figure 3 that a good *empirical* correlation of the sparse exact data is given by $F(j) \to (2j+7)/(j+8)$; the errors in δ_{cr} on this basis are now never greater than $\frac{1}{2}\%$ over the entire range of shapes considered.

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Appendix 1. Symbols and nomenclature

Frequently occurring symbols, their significance and their dimensions are listed below. Other symbols have only local relevance. It should be noted that in appendix 2 the symbols have only the *geometric* meanings there conferred.

Symbol and significance	*dimensions*
$a = a(\Theta, \phi)$, distance from body centre to surface in the direction (Θ, ϕ)	m
a_0 a characteristic dimension, value of a in a special direction	m
A effective first-order pre-exponential (frequency) factor	s^{-1}
$b_n(j)$ shape dependent coefficients defined by (3.16) and giving the Frank-Kamenetskii temperature profiles (3.22)	—
$Bi = hR_S = 3HV/\kappa S$ the Biot number	—
c specific heat of reactant mixture	$J\,kg^{-1}\,K^{-1}$
$D = \kappa/\sigma c$, thermal diffusivity of reactant mixture	$m^2\,s^{-1}$
E Arrhenius activation energy	$J\,mol^{-1}$
$F = (2j+6)/(j+7) \simeq \frac{1}{3}\delta_{cr}(R_0, Bi = \infty)$, a shape factor (see § 4 (*a*))	—
$h = H/\kappa$, a measure of the surface heat transfer coefficient	m^{-1}
H the surface heat transfer coefficient	$W\,m^{-2}\,K^{-1}$
$j = 3\chi - 1$, a shape factor reducing to 0, 1, 2 for ∞ slab, ∞ cylinder and sphere, respectively (see (3.19))	—
$l = a\cos\Psi$, distance from body centre to tangent plane	m
n coordinate directed along outward normal to surface	m
q exothermicity per unit mass of reactant mixture	$J\,kg^{-1}$
$\boldsymbol{r}$ radius vector from origin (body centre) to arbitrary point	m
$r = \lvert\boldsymbol{r}\rvert$, distance from origin	m
R_{eq} radius of equivalent sphere under specified boundary conditions (for definition see § 5 (*b*))	m
$R_S = R_{eq}(Bi \to 0) = 3V/S$, the Semenov radius (see § 2)	m
$R_{FK} = R_{eq}(Bi \to \infty)$, the Frank-Kamenetskii radius (see § 4 (*b*))	m
$\boldsymbol{R}$ the universal gas constant	$J\,mol^{-1}\,K^{-1}$

Symbol and significance	*dimensions*
$R_0 \simeq R_{FK}$, a mean radius, $R_0^{-2} = \frac{1}{4\pi}\iint a^{-2}\,d\omega$	m
S the reactant surface (or its total area)	m^2
dS an element of the surface	m^2
t time	s
$t_{th} = (D\lambda_1)^{-1}$, the quasistationary thermal relaxation time	s
T absolute temperature	K
T_a ambient temperature	K
V the reactant bulk (or its total volume)	m^3
dV an element of volume	m^3
$X = \exp[\frac{1}{2}(\theta_0 - \theta)]$, a measure of temperature (see §3(*c*))	—
$X_1 = \exp[\frac{1}{2}\theta_0]$	—
y the parameter of the generalized Frank-Kamenetskii solutions (3.22); see also (3.12)	—
$\beta = 9Bi/10e = (27/10e)(HV/\kappa S)$, a modified Biot number	—
$\gamma = q\sigma EA \exp(-E/\boldsymbol{R}T_a)/\kappa \boldsymbol{R}T_a^2$, a measure of heat evolution rate	m^{-2}
$\gamma_l = e^{-1}\Gamma_m^{-1}$, a lower bound on γ_{cr} (see §6(*b*))	m^{-2}
$\gamma_u = e^{-1}\lambda_1$, an upper bound on γ_{cr} (see §6(*a*))	m^{-2}
Γ the solution of the Poisson equation (6.8)	m^2
Γ_m the maximum value of Γ in V; (Poisson length)^2	m^2
$\delta(a_0) = \gamma a_0^2$, Frank-Kamenetskii's dimensionless parameter based on the length a_0	—
$\delta = \delta(R_0)$, a generalized form of Frank-Kamenetskii's δ	—
$\epsilon = \boldsymbol{R}T_a/E$, the reduced ambient temperature	—
$\theta = E(T - T_a)/\boldsymbol{R}T_a^2$, Frank-Kamenetskii's reduced temperature excess	—
θ_0 reduced central temperature excess	—
$\theta_{ad} = qE/c\boldsymbol{R}T_a^2$, reduced adiabatic temperature rise	—
$\bar{\theta} = V^{-1}\iiint \theta\,dV$, the spatially averaged temperature excess	—
θ_i the eigenfunctions of the associated Helmholtz equation (6.2), (6.3)	—
Θ the colatitude of spherical polar coordinates	—
κ the thermal conductivity of the reactant mixture	$W\,K^{-1}\,m^{-1}$
λ_i the eigenvalues of the Helmholtz equation (6.2), (6.3)	m^{-2}
λ_1 = (Helmholtz length)$^{-2}$, the principal (least) eigenvalue of (6.2), (6.3)	m^{-2}
$\rho = r/a(\Theta, \phi)$, reduced distance from body centre	—
$P = R_{eq}/R_S$, reduced equivalent sphere radius	—
σ density of reactant mixture	$kg\,m^{-3}$
ϕ the longitude of spherical polar coordinates	—
$\Phi = (R_{FK}/R_S)^2 = 5(j+1)(j+7)/27(j+3)$, a measure of the variation of R_{eq} with Bi, see §4(*b*)	—
$\chi = R_0^2/R_S^2$, a dimensionless shape parameter	—

Symbols and significance	*dimensions*
$\psi = \gamma\kappa R_S/3H = \delta(R_S)/3Bi$, the Semenov criterion (see § 2)	—
$\psi_u = \gamma_u\kappa R_S/3H$, an upper bound on ψ_{cr}	—
Ψ the angle between radius vector and surface normal (see figure 1)	—
ω solid angle; $d\omega = \sin\Theta\, d\Theta\, d\phi$	—

Subscripts

cr, critical value

eq, equivalent

sph, value pertaining to the sphere

Appendix 2. Some important geometrical properties of convex geometries

A 2 (*a*). *Evaluation of the Semenov equivalent sphere radius* (R_S)

The Semenov equivalent sphere radius R_S is by definition $3V/S$ and thus, for many simple geometries, can be evaluated using tabulated expressions for V and S. When tabulated results are not available the results given below may be used. Their most important feature is that R_S is essentially the harmonic mean of the three principal dimensions of the body.

In general our surface is specified by an expression of the form $r = a(\Theta, \phi)$ where r, Θ, ϕ are spherical polar coordinates whose origin and orientation are arbitrary, but often conveniently related to symmetry features of the surface S. The total surface area and total volume are given by

$$V = \frac{1}{3}\iint a^3\, d\omega = \frac{1}{3}\iint a^3 \sin\Theta\, d\Theta\, d\phi,$$

$$S = \iint a^2 \sec\Psi\, d\omega = \iint a^2 \sec\Psi \sin\Theta\, d\Theta\, d\phi,$$

where Ψ is the angle between the radius vector and the outward surface normal:

$$\sec^2\Psi = 1 + \left[\frac{1}{a}\frac{\partial a}{\partial\Theta}\right]^2 + \left[\frac{1}{a\sin\Theta}\frac{\partial a}{\partial\phi}\right]^2.$$

The following particular results are useful

(i) *Symmetric bodies of rotation*, $a = a(\Theta) = a(\Theta + \pi)$

$$R_S = \int_0^{\frac{1}{2}\pi} a^3 \sin\Theta\, d\Theta \Big/ \int_0^{\frac{1}{2}\pi} a\left\{a^2 + \left(\frac{da}{d\Theta}\right)^2\right\}^{\frac{1}{2}} \sin\Theta\, d\Theta.$$

(ii) *Polyhedra*

Let S consist of a number of plane surfaces S_i which are distant by l_i from some arbitrary centre O. Then

$$R_S^{-1} = \frac{\Sigma S_i}{\Sigma l_i S_i}.$$

This formula remains valid if some of the surfaces S_i are spherical (cylindrical) so long as the distance from O of all the tangent planes of a given surface S_i have the constant value l_i. If a centre O is found such that l_i has the same value l for all surfaces S_i, then the simple result $R_S = l$ emerges.

(iii) *Right cylinders*

Let the height be $2h$ and let the cross-section have area A and perimeter p. Then $V = 2Ah$, $S = 2(A+hp)$ and

$$3R_S^{-1} = h^{-1} + 2r_0^{-1},$$

where r_0 is a mean radius of the cross-section

$$r_0 = 2A/p = \frac{\oint l_0\,\mathrm{d}s}{\oint \mathrm{d}s} = \langle l_0 \rangle_S,$$

which is seen to be the average value of the distance l_0 of the tangent plane at the perimeter from any centre.

If the cross-section is rectangular we have the case of a rectangular brick $(2a \times 2b \times 2c)$ and we find $r_0^{-1} = \frac{1}{2}(b^{-1}+c^{-1})$, and

$$R_S^{-1} = \tfrac{1}{3}[a^{-1}+b^{-1}+c^{-1}].$$

The latter result illustrates well the salient feature of all expressions for R_S: that when some principal dimension of a body is large by comparison with some orthogonal dimension then the former has little influence on the value of the Semenov radius.

A 2(*b*). *Evaluation of the effective size or mean radius*, R_0

Definition

The effective size is defined by the relation

$$R_0^{-2} = \frac{1}{4\pi}\iint a^{-2}\,\mathrm{d}\omega = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi} a^{-2}\sin\Theta\,\mathrm{d}\Theta\,\mathrm{d}\phi,$$

where $r = a(\Theta, \phi)$ defines the outer surface and r, Θ, ϕ are spherical polar coordinates with origin at the centre of the body. This relation takes on a simple form for certain rather general shapes:

A 2(*b*) (i). *Expressions for symmetric geometries*

Bodies of rotation. $\partial a/\partial\phi = 0$, $a(\pi+\Theta) = a(\Theta)$,

$$R_0^{-2} = \int_0^{\frac{1}{2}\pi} a^{-2}\sin\Theta\,\mathrm{d}\Theta.$$

Right cylinders of arbitrary cross-section, height $2h$, cylindrical surface

$$r = a_0(\phi)\,\mathrm{cosec}\,\Theta, \quad \Theta_0 = \tan^{-1}[a_0(\phi)/h]$$

$$3h^2R_0^{-2} = 1 + \frac{1}{\pi}\int_0^{2\pi}\cos^3\Theta_0\,\mathrm{cosec}^2\,\Theta_0\,\mathrm{d}\phi.$$

When the cylinder is infinite $(a_0/h \to 0)$ this relation reduces to

$$R_0^{-2} = \tfrac{2}{3}\langle a_0\rangle^{-2}$$

where the mean cross-sectional radius $\langle a_0 \rangle$ is given by

$$\langle a_0\rangle^{-2} = \frac{1}{2\pi}\int a_0^{-2}\,\mathrm{d}\phi.$$

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Bipyramids. Vertices at $z = \pm h$, $x = y = 0$; base $z = 0$, $r = a_0(\phi)$; upper surface

$$r^{-1} = h^{-1}\cos\Theta + a_0^{-1}\sin\Theta$$

$$3R_0^{-2} = h^{-2} + \frac{1}{\pi}\int_0^{2\pi} a_0^{-2}\,\mathrm{d}\phi + \frac{1}{\pi h}\int_0^{2\pi} a_0^{-1}\,\mathrm{d}\phi.$$

A 2 (*b*) (ii). *Contributions to* R_0^{-2} *of commonly encountered surfaces*

Many surfaces of interest are composed wholly or in part of plane, spherical or cylindrical surfaces, so that it is useful to know their contribution

$$I_\mathrm{i} = \frac{1}{4\pi}\iint_S a^{-2}\,\mathrm{d}\omega \quad \text{to} \quad R_0^{-2}.$$

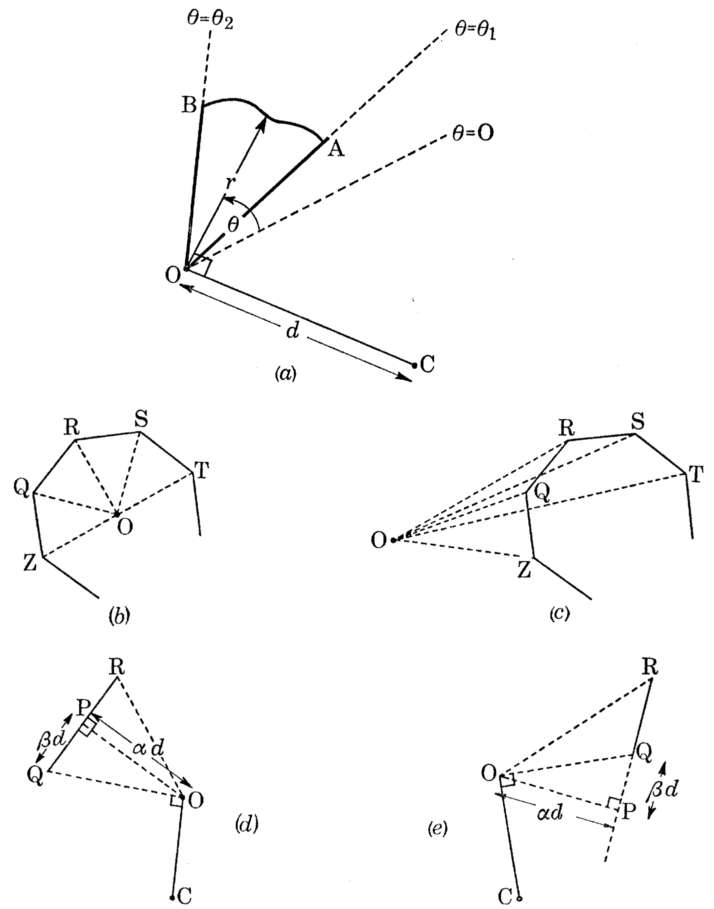

FIGURE 5. The configuration of planar and polygonal facets. The foot of the perpendicular from the body centre C to the plane of the facet is point O, where OC = *d*. (*a*) an arbitrary contour AB; (*b*) and (*c*) decomposition of polygonal facet into triangles; (*d*) and (*e*) decomposition of triangles into basic right-angled triangles.

Contribution of a general plane surface. Configuration (see figure 5 (*a*)). The perpendicular from the body centre C meets the plane at O, OC = *d*. O is the origin of the polar coordinates (r, θ) specifying a boundary curve $r(\theta)$ along which θ varies monotonically. The contribution I_1 of the area bounded by $r = r(\theta)$ and its terminal radii, $\theta = \theta_1$, $\theta = \theta_2$ is given below.

$$12\pi\,d^2 I_1 = \theta_2 - \theta_1 - \int_{\theta_1}^{\theta_2}(1+\rho^2)^{-\frac{3}{2}}\,\mathrm{d}\theta,$$

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where $\rho = r/d$. The contribution I from a *surface bounded by any closed contour* may be found by compounding integrals of the type I_1 with an appropriate choice of sign.

In particular *if the contour is a circle*, centre O, radius r_0 we have

$$6d^2 I_1 = 1-(1+\rho_0^2)^{-\frac{3}{2}}; \quad \rho_0 = r_0/d.$$

Contribution of polygonal plane surface. Any plane polygon QRST...ZQ may be decomposed into the triangles $\pm$OQR, $\pm$ORS, $\pm$OST, ..., $\pm$OZQ (see figures 5(*b*) and 5(*c*)) and each such triangle comprises two right-angled triangles, e.g. OQR = OPQ $\pm$ OPR, where P is the foot of the perpendicular from O onto QR (see (*d*) and (*e*) of figure 5). Thus I for the polygonal facet is the algebraic sum of contributions I_2 from each basic right-angled triangle of the type OPQ (of which there are $2n$ for an n-gon facet). With the notation OC = d, OP = αd, PQ = βd, $\angle$OPQ = $\frac{1}{2}\pi$, we have for the contribution to R_0^{-2} of the basic right-angled triangle OPQ:

$$12\pi d^2 I_2(\mathrm{OPQ}) = \tan^{-1}\left(\frac{\beta}{\alpha}\right) - \tan^{-1}\left\{\frac{\beta}{\alpha\sqrt{(1+\alpha^2+\beta^2)}}\right\} + \frac{\alpha\beta}{(1+\alpha^2)\sqrt{(1+\alpha^2+\beta^2)}}.$$

By combining two such expressions we find the integral I_3 for a rectangle of sides a and b lying in a plane distant by c from the body centre C and having one of its corners at O:

$$12\pi c^2 I_3(\mathrm{OPQR}) = \tan^{-1}\lambda + \mu,$$

where

$$\mu = \frac{\Pi(a)}{\Pi(a^2+b^2)\sqrt{(\Sigma a^2)}}(a^2+b^2)(c^2+\Sigma a^2),$$

$$\lambda = \Pi(a)/c^2\sqrt{\Sigma a^2)}$$

$$\Sigma a = a+b+c, \text{ etc.}; \ \Pi(a) = abc, \text{ etc.}$$

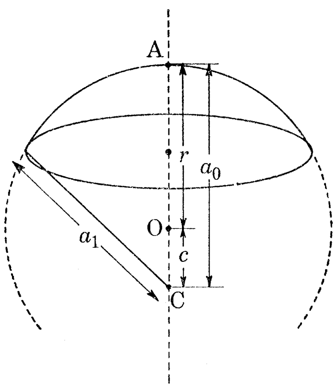

FIGURE 6

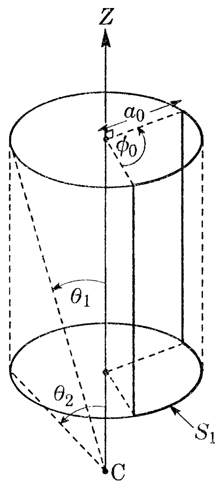

FIGURE 7

FIGURE 6. The spherical cap configuration. C-body centre, O-sphere centre, A-pole of sphere.
FIGURE 7. Cylindrical surface configuration. The body centre C lies on the axis of the cylinder of which S_1 is part of the surface.

Contribution of spherical cap. The configuration considered (see figure 6) is a cap of a sphere centre O, radius r, pole A with the body centre C lying on the polar axis, OC = c. Distance of pole from O = $a_0 = c+r$, distance from rim to C = a_1. The contribution to R_0^{-2} is given by

$$I = \frac{1}{12c}\left[a^{-3}(3a^2+r^2-c^2)\right]_{a_0}^{a_1}.$$

Contribution of a cylindrical surface. For simplicity we consider the configuration shown in figure 7 in which the surface S_1, whose contribution we require, is bounded by lines of constant θ and constant ϕ. The contribution of S_1 to R_0^{-2} is given by

$$I_1 = \frac{\phi_0}{4\pi}\left[\cos\theta - \tfrac{1}{3}\cos^3\theta\right]_{\theta_2}^{\theta_1} a_0^{-2}.$$

A 2 (*b*) (iii). *Explicit expressions for the mean radius R_0 for simple geometries*

Although the mean radius R_0 is readily evaluated for many simple geometries from its definition and from the ancillary results given above, the evaluation usually involves lengthy algebraic manipulation. We therefore set out below a convenient tabulation of expressions for R_0^{-2} covering a wide range of the geometries practically encountered.

(1). Bodies of rotation (about z-axis),

$$R_0^{-2} = \int_0^{\frac{1}{2}\pi} a^{-2}(\Theta)\sin\Theta\,\mathrm{d}\Theta.$$

(1.1). Elliptical section, $x^2a^{-2}+z^2c^{-2} = 1$ (*ellipsoid of rotation*);

$$3R_0^{-2} = 2a^{-2}+c^{-2}.$$

(1.11). Circular section—*the sphere*, $a = c$,

$$R_0 = a.$$

(1.2). Rectangular section—*the finite right circular cylinder* (geometry (2.1) with $n = \infty$), height $2d$, radius a,

$$3R_0^{-2} = d^{-2}+2[1+a^2/d^2]^{-\frac{1}{2}}a^{-2}.$$

(1.21). Square section—*the equicylinder*, $d = a$,

$$3a^2R_0^{-2} = 1+\surd 2 = 2.414.$$

(1.3). Diamond section—*the bicone*, radius of base $= l$, height $= 2h$ (geometry (3.1) with $n = \infty$),

$$3R_0^{-2} = h^{-2}+2l^{-2}+2(hl)^{-1} = h^{-2}+2[1+l/h]\,l^{-2}.$$

(1.31). Bicone with diameter = total height, $l = h$,

$$3l^2R_0^{-2} = 5.$$

(1.4). Shapes involving spherical surfaces, see (5)

(2). Right cylinders (prisms).

(2.1). *Regular n-gon base.* Height $= 2d$, radius of basal incircle $= a$

$$R_0^{-2} = (n/3\pi)\,a^{-2}\,[(\pi/n)\,t^2+(\cos^2(\pi/n)+t^2)\,Z+(1-t^2)\tan^{-1}Z],$$

where $t = a/d, \quad Z = \tan(\pi/n)\,[1+t^2\sec^2(\pi/n)]^{-\frac{1}{2}} \quad (n = 3, 4, 5, \ldots).$

(2.11). *Infinite polygonal cylinder*, $d/a \to \infty$,

$$R_0^{-2} = \frac{1}{3a^2}\left[1+\frac{n}{2\pi}\sin\frac{2\pi}{n}\right].$$

(2.12). *Thin polygonal cylinder*, $a/d \to \infty$,

$$R_0^{-2} = 1/3d^2.$$

(2.13). *Equicylinder*, $a = d$ $$3a^2R_0^{-2} = 1+\left[\frac{(2+\tau^2)^{\frac{1}{2}}}{1+\tau^2}\right]\left[\frac{\tau}{\tan^{-1}\tau}\right],$$
where $\tau = \tan(\pi/n)$.

(2.14). *Circular base* ($n = \infty$) (see (1.2)).

(2.2). *Rectangular base*. See rectangular brick, (4.1).

(2.3). Diamond base—*the biprism or double wedge* (perpendicular diagonals of half lengths a, b). Height $2d$.

$$\tfrac{3}{2}\pi\, d^2R_0^{-2} = \tfrac{1}{2}\pi + (\alpha^{-2}+\beta^{-2}-1)\tan^{-1}\mu + (\alpha\beta)^{-1}\{\surd(1+\alpha^2)+\surd(1+\beta^2)\},$$

where $$\alpha = a/d,\ \beta = b/d,\ \mu = \alpha\beta\left\{\frac{\surd(1+\alpha^2)}{\alpha^2}+\frac{\surd(1+\beta^2)}{\beta^2}\right\}\{\surd(1+\alpha^2)\surd(1+\beta^2)-1\}^{-1}.$$

(2.31). *Infinite biprism or double wedge*, $d \to \infty$.

$$3R_0^{-2} = a^{-2}+b^{-2}+(4/\pi)(ab)^{-1}.$$

(3). Bipyramids. Height $2h$.

(3.1). *Regular n-gon base* (radius of basal incircle $= l$),

$$R_0^{-2} = \tfrac{1}{3}h^{-2}+\frac{1}{3}\left(1+\frac{n}{2\pi}\sin\frac{2\pi}{n}\right)l^{-2}+\frac{2}{3}\frac{n}{\pi}\sin\left(\frac{\pi}{n}\right)(hl)^{-1}.$$

(3.11). *Regular octahedron*, $n = 4$, $h = \surd 2\, l$, length of edges $= 2l$,

$$l^2R_0^{-2} = \tfrac{1}{2}+2/\pi = 1.1366.$$

(4). Polyhedra

(4.1). *Rectangular brick* ($2a\times 2b\times 2c$),

$$\tfrac{3}{2}\pi\, R_0^{-2} = \Sigma\{a^{-2}\tan^{-1}(\Phi a^{-2})\}+\Psi,$$

where $$\Phi = \Pi(a)/\surd(\Sigma a^2),$$

$$\Psi = \Pi(a)\surd(\Sigma a^2)\,[\Sigma a^2\,\Sigma a^{-2}-1]/\Pi(a^2+b^2),$$

and $$\Pi(a) = abc \text{ etc.},\quad \Sigma(a) = a+b+c \text{ etc.}$$

(4.11). *Infinite rectangular rod* ($c \to \infty$),

$$\tfrac{3}{2}\pi\, R_0^{-2} = a^{-2}\tan^{-1}\frac{b}{a}+b^{-2}\tan^{-1}\frac{a}{b}+(ab)^{-1}.$$

(4.111). *Infinite square rod* ($c\to\infty$, $a = b$),

$$3a^2R_0^{-2} = 1+2/\pi = 1.6366.$$

(4.12). *Square brick* ($a = c$, $b = ta$),

$$\tfrac{3}{2}\pi\, a^2R_0^{-2} = \tan^{-1}\mu+t^{-2}\tan^{-1}(\mu^{-1})+\mu t^{-2},$$
where $\mu = t\surd(2+t^2)$.

(4.121). *Cube* ($t = 1$), $\mu = \surd 3$

$$3a^2R_0^{-2} = 1+2\surd(3)/\pi = 2.1027.$$

(4.13). *Infinite slab* ($a \to 0$) $\qquad 3R_0^{-2} \to a^{-2}$.

(4.2). *Right cylinders*. See (2).

(4.3). Regular tetrahedron (side $2a$, radius of insphere $= \frac{1}{2}\sqrt{(\frac{2}{3})}\,a$)

$$a^2R_0^{-2} = 2+(8/3\pi)\sqrt{3} = 3.4702.$$

(4.4). *Regular octahedron* (side $2a$)

$$a^2R_0^{-2} = \tfrac{1}{2}+2/\pi = 1.1366.$$

(5). SHAPES INVOLVING SPHERICAL SURFACES

(5.1). *Finite circular cylinder with spherical caps.* Cylindrical part: radius c, height $2h$. Caps: radius r, height l, distance from centre of sphere to centre of cylinder $= b = h-\sqrt{(r^2-c^2)}$

$$R_0^{-2} = \cos\alpha\left[\frac{1}{c^2}+\frac{2}{3hb}\right]-\tfrac{1}{3}\cos^3\alpha\left[\frac{1}{c^2}+\frac{1}{h^2}\right]+\frac{1}{3(h+l)^2}\left[1-\frac{2(1+l/h)}{b/h}\right],$$

where $\alpha = \tan^{-1}(c/h)$ and $c^2 = l(2r-l)$.

(5.11). *Finite circular cylinder with hemispherical caps*, $r = c = l$, $b = h$

$$3c^2R_0^{-2} = 2\sqrt{(1+t^2)}-\frac{(1+2t)}{(1+t)^2}t^2,$$

where $t = \tan\alpha = c/h$.

(5.12). *Biconvex lens*, $h = 0$. Radius of curvature r, aperture $2c$, thickness $2l$.

$$l^2R_0^{-2} = \frac{1}{3}\frac{1+3\gamma^{-1}+6\gamma^{-2}}{1+3\gamma^{-1}+2\gamma^{-2}} = \frac{1+\frac{1}{2}\gamma+\frac{1}{6}\gamma^2}{1+\frac{3}{2}\gamma+\frac{1}{2}\gamma^2},$$

where $\gamma = (c/l)-1$, $2r = [2+2\gamma+\gamma^2]\,l$.

(5.121). *Thick lens* (quasi-spherical), $c \to l$,

$$l^2R_0^{-2} = 1-\gamma \quad (\gamma \ll 1).$$

(5.122). *Thin lens* $(\gamma \to \infty)$, $\quad 3l^2R_0^{-2} = 1+4\gamma^{-2}.$

(6). MISCELLANEOUS GEOMETRIES

(6.1). *Ellipsoids*, $x^2a^{-2}+y^2b^{-2}+z^2c^{-2} = 1$,

$$3R_0^{-2} = a^{-2}+b^{-2}+c^{-2}.$$

(6.11). *Ellipsoid of revolution*, $a = b$, $\quad 3R_0^{-2} = 2a^{-2}+c^{-2}.$

(6.12). *Sphere*, $a = b = c$, $\quad R_0 = a.$

(6.13). Truncated ellipsoid of revolution (*ellipsoidal barrel*). Height $2l$, principal radius b, radius at planes of truncation $= a$,

$$3R_0^{-2} = l^{-2}+\frac{2}{\sqrt{(1+a^2/l^2)}}b^{-2}.$$

(6.14). *Infinite ellipsoidal cylinder*, $c \to \infty$,

$$3R_0^{-2} = a^{-2}+b^{-2}.$$

APPENDIX 3. VALIDITY OF THE STEADY-STATE APPROXIMATION

The steady-state equation (3.1) does not constitute an exact description of real systems but it does generate asymptotically correct results for systems of large activation energy E and exothermicity q. We indicate below how our results are to be modified when q and E are small or when ambient temperatures are high. All steady-state approximations are subject to such modifications.

A 3 (*a*). *Low activation energy*

Our derivation of the criticality criterion has as its starting-point not the exact steady-state heat balance equation (3.1) but (3.4), in which Frank-Kamenetskii's exponential approximation has been invoked. In order that this be a good approximation we must have

$$\epsilon \equiv RT_a/E \ll 1, \tag{A 3.1}$$

so that the error involved becomes important if the activation energy is less than *ca.* 40 kJ mol^{-1}. An exact general treatment of the correction to be applied to δ_{cr} when ϵ is non-zero is beyond the present scope, but the following serves as a useful guide.

(*a*) The numerical results of Parks (1961) for class A geometries and for the cube and equicylinder under conditions of infinite Biot number are all fitted by an expression of the form

$$\delta_{cr}(\epsilon) = \delta_{cr}(\epsilon = 0)\,[1 + A\epsilon], \tag{A 3.2}$$

where $A = 1.07 \pm 0.04$, $\epsilon \leqslant 0.05$.

(*b*) Semenov's classical approach (1928) is valid for an arbitrary temperature dependence of reaction rate (in the limit of small Biot number). Adopting the Arrhenius form, we obtain the following expression, which is exact for all geometries,

$$\frac{\psi_{cr}(\epsilon)}{\psi_{cr}(\epsilon = 0)} = \frac{\delta_{cr}(\epsilon)}{\delta_{cr}(\epsilon = 0)} = \theta_m\, e^{-\epsilon\theta_m}, \tag{A 3.3}$$

where $$\theta_m = [1 - 2\epsilon - \surd(1 - 4\epsilon)]/2\epsilon^2 = 1 + 2\epsilon + 5\epsilon^2 + O(\epsilon^3).$$

When ϵ is small we may expand (A 3.3) to give

$$\frac{\delta_{cr}(\epsilon)}{\delta_{cr}(\epsilon = 0)} = 1 + \epsilon + \tfrac{3}{2}\epsilon^2 + O(\epsilon^3), \tag{A 3.4}$$

In view of the close similarity of (A 3.2) and (A 3.4), which apply to opposite extremes of the heat transfer coefficient, we conjecture that (A 3.4) or even (A 3.3) may be used to allow for the effect of finite activation energy with little resultant error for any Biot number and for any geometry, at least when ϵ is small. Barzykin *et al.* (1964) have shown numerically that this result is a good approximation for the class A geometries.

A 3 (*b*). *Low exothermicity: reactant consumption*

Our entire treatment above is concerned with the steady state and thus assumes that reactant consumption is negligible. In order to observe a near-critical steady state at the ambient temperature T_a it is necessary that there be a time t which is at once much greater than the thermal relaxation time t_{th} of the system and much less than the half life $t_{\frac{1}{2}}$ of the reaction at $T_{a,cr}$. Only then can the reactant temperature be brought from a low value to the neighbourhood of $T_{a,cr}$ without significant reactant consumption. Now for any geometry and any value of the heat transfer coefficient we know from §§ 6 (*a*) and 7 (*b*) that

$$t_{th} \sim \frac{\sigma c}{\kappa \lambda_1}, \quad t_{\frac{1}{2}} \sim [A \exp(-E/RT_a)]^{-1}, \quad \gamma_{cr} \sim e^{-1}\lambda_1,$$

where $\lambda_1^{-\frac{1}{2}}$ is an effective size (the Helmholtz length, see § 6 (*a*)) and c is the heat capacity of the reactant. Thus a necessary condition for negligible reactant consumption, $t_{th} \ll t_{\frac{1}{2}}$, in a near critical régime may be written as

$$\left(\frac{t_{th}}{t_{\frac{1}{2}}}\right)_{cr} \sim \left[\frac{\sigma c A \exp\left[-E/RT_a\right]}{\kappa \lambda_1}\right]_{cr} = \left(\frac{\gamma_{cr}}{\lambda_1}\right)\left(\frac{cRT_a^2}{qE}\right) \simeq e^{-1}\,\theta_{ad}^{-1} \ll 1,$$

i.e.

$$\theta_{ad} \equiv \frac{qE}{cRT_a^2} \gg 1. \tag{A 3.5}$$

This generally valid condition agrees with those more precise conditions derived elsewhere for simple geometries (Barzykin *et al.* 1964) and for very small Biot numbers (Todes & Melent'ev 1939; Frank-Kamenetskii 1945; Gray & Lee 1967*b*; Adler & Enig 1964*a*). In essence, unless a large temperature rise q/c accompanies complete *adiabatic* reaction, reactant consumption will be significant at criticality under any conditions. Our steady-state treatment ignores reactant consumption and thus tacitly assumes that $\theta_{ad} \to \infty$. In order to make crude allowance for reactant consumption we note that the expression

$$\frac{\delta_{cr}(\epsilon, \theta_{ad})}{\delta_{cr}(\epsilon, \theta_{ad} = \infty)} = \frac{1-4\epsilon}{1-4(\epsilon+\theta_{ad}^{-1})}, \tag{A 3.6}$$

where $\delta_{cr}(\epsilon, \theta_{ad} = \infty)$ is given by (A 3.3), is a rough fit over a wide range of ϵ and θ_{ad}^{-1} to known data (Barzykin *et al.* 1964, Adler & Enig 1964*a, b*) for a number of particular cases in which the kinetics are first order.

A 3 (*c*). *High ambient temperature*

Both conditions (A 3.1) and (A 3.5) impose upper limits on the range of ambient temperatures for which the steady-state results remain accurate.

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