Fire Research Note

No. 821

THE EFFECT OF REACTANT CONSUMPTION ON SUBSTANTIALLY SUB-CRITICAL SELF-HEATING

by

P. C. BOWES

May 1970

FIRE
RESEARCH
STATION

F.R.Note No 821
May 1970

THE EFFECT OF REACTANT CONSUMPTION ON SUBSTANTIALLY SUB-CRITICAL SELF-HEATING

by

P. C. Bowes

SUMMARY

Measurements of the maximum temperature increase in self-heating solids under substantially sub-critical conditions provide useful estimates of rates of heat generation at different temperatures. The purpose of this paper is to calculate theoretically the extent to which these estimates are affected by consumption of reactant during self-heating.

It is confirmed that the effect of reactant consumption in this region is considerably less than its effect on the critical condition for thermal explosion. For systems having a heat of reaction high enough to permit sharply defined thermal explosion, the effect of reactant consumption on substantially sub-critical self-heating can be to reduce the maximum temperature by less than 10 per cent.

KEY WORDS: Spontaneous heating, Self-heating.

MINISTRY OF TECHNOLOGY AND FIRE OFFICES' COMMITTEE
JOINT FIRE RESEARCH ORGANIZATION

LIST OF SYMBOLS

A = Pre-exponential factor of Arrhenius equation

a = $\beta'/\rho\delta$

B = dimensionless adiabatic temperature rise (equation (9))

c = specific heat

E = activation energy

h = surface heat transfer coefficient (convection + radiation)

j = 0, 1, 2 respectively for infinite plane slab, infinite cylinder and sphere

k = rate constant

K = thermal conductivity

n = order of reaction

p = $1 + \theta'_o$ = constant

Q = heat of reaction per unit mass

r = semi-thickness of slab, radius of cylinder or sphere

T = absolute temperature, subscripts o and A refer respectively to centre and ambient

t = time

α = dimensionless surface heat transfer coefficient (equation (5))

β = dimensionless effective heat transfer coefficient

β' = $\beta(j + 1)$

δ = dimensionless self-heating parameter (equation (4))

θ = dimensionless temperature increase above ambient
Subscript o refers to centre of body, s to surface

θ'_o = small constant value of θ_o

ρ = density

τ = dimensionless time (equation (8))

w = residual fraction of reactant $1 \geqslant w \geqslant 0$

z = dimensionless distance from centre of slab, infinite cylinder or sphere.

F.R.Note No 821
May 1970

THE EFFECT OF REACTANT CONSUMPTION ON SUBSTANTIALLY SUB-CRITICAL SELF-HEATING

by

P. C. Bowes

INTRODUCTION

The effect of reactant consumption on the critical condition for thermal explosion, and on immediately sub-critical temperature maxima, is now well established[1-3*]. For realistic cases, reactant consumption can increase the value of the critical explosion parameter, and estimates of rates of heat evolution based on experimental thermal explosion data, by a factor of up to about 2; beyond this, sharply defined explosion, or ignition, tends to disappear.

A study of substantially sub-critical temperature maxima in practical cases of self-heating and ignition can provide a check on the applicability of the simple thermal explosion model and, in particular, yield information on subsidiary self-heating reactions[4]. Furthermore, it has been successfully exploited as a calorimetric method, for slow self-heating, by Walker and his associates[5,6]. So far, however, it appears that no numerical estimates have been published of the effect of reactant consumption on the temperature increase in this substantially sub-critical region. In view of the practical usefulness of this region, such estimates are desirable, and are the objective of this paper. These estimates require no more than an extension of existing procedures for near-critical self-heating, with considerable simplification made possible by the smallness of the temperature increases involved.

---

*Reference 1 compares analytical results; recent numerical results are given in references 2 and 3. References to earlier work will be found in these.

THEORETICAL

The case to be discussed is self-heating in a solid of finite thermal conductivity with heat loss by convection and radiation to surroundings at constant temperature. It will be assumed that heat is generated by a reaction which is of order n and whose rate varies with temperature in accordance with the Arrhenius equation. It will be convenient to work in terms of the usual dimensionless quantities of current thermal explosion theory (see list of symbols and below).

It is convenient, first, to state the result for small steady-state temperature increases due to self-heating when reactant consumption can be neglected (zero order reaction)*.

For this case, and the boundary condition

$$-\frac{d\theta_s}{dz} = \alpha \theta_s \qquad \ldots (1)$$

it can be shown[4] that the central temperature increase is given by

$$\theta_o = \frac{\delta}{2(j+1)} \cdot \frac{2+\alpha}{\alpha} e^{\theta_o} \qquad \ldots (2)$$

where $j = 0$, 1 or 2 respectively for a plane slab, infinite cylinder or sphere and, as usual,

$$\theta = \frac{E}{RT_A^2}(T - T_A) \qquad \ldots (3)$$

$$\theta = \theta_o \text{ when } T = T_o$$

$$\delta = \frac{E}{RT_A^2} \cdot \frac{r^2 Q A e^{-E/RT_A}}{K} \qquad \ldots (4)$$

$$\alpha = hr/K \qquad \ldots (5)$$

---

*A number of theoretical relationships are available for this case, differing principally in the degree of approximation applied to the Arrhenius relationship[4-9].

Equation (2) is based on Benson's assumption[7] of a reaction rate independent of temperature over a small range of temperature and gives values of θ_o slightly higher than Chambré's more accurate analysis[10] employing Frank-Kamenetskii's exponential approximation to the Arrhenius relationship. By inspection (Fig.2 of ref.4), the error in θ_o given by equation (2) is about 15 per cent when $\theta_o = 0.4$ and about 5 per cent when $\theta_o = 0.2$.

Using the "effective transfer" approximation[11,12] for the conduction term and the linear approximation for the exponential, e^{θ} (c.f. Wilson[8]), the equations governing self-heating for a reaction of order n with respect to the fraction of residual reactant, w, are

$$\frac{d\theta_o}{d\tau} = \delta w^n(1 + \theta_o) - \beta'\theta_o \qquad \ldots(6)$$

$$\frac{dw}{d\tau} = -\frac{\delta}{B} w^n(1 + \theta_o) \qquad \ldots(7)$$

where

$$\tau = Kt/\rho c r^2 \qquad \ldots(8)$$

$$B = \frac{E}{RT_A^2} \cdot \frac{Q}{\rho c} \qquad \ldots(9)$$

$$\beta' = \beta(j + 1)$$

β is the effective heat transfer coefficient and has to be evaluated (see below).

For $\theta_o \ll 1$, (as is appropriate here) it is possible to write $1 + \theta_o' = p$ = constant, where θ_o' is assigned a small constant value θ_o'. Using this simplification, a simple solution is readily obtainable for the case of a first order reaction, $(n = 1)$, as follows.

Integration of equation (7), with $n = 1$, for the initial condition $w = 1$ when $\tau = 0$, and substitution into equation (6) gives

$$\frac{d\theta_o}{d\tau} = p\delta e^{-p\delta\tau/B} - \beta'\theta_o \qquad \ldots(10)$$

This may be integrated (initial condition $\theta_o = 0$ when $\tau = 0$) to give

$$\theta_o = \frac{B}{Ba - 1}\left(e^{-\beta'\tau/Ba} - e^{-\beta'\tau}\right) \qquad \ldots(11)$$

where

$$a = \beta'/p\delta$$

θ_o can be shown to have a maximum value, $\theta_{o\,max}$, when $\tau = \tau_m$

where

$$\tau_m = \frac{Ba}{\beta'(Ba - 1)} \log_e Ba \qquad \ldots(12)$$

Substitution of equation (12) into equation (11) gives

$$\theta_{o\,max} = B(Ba)^{-\frac{Ba}{Ba-1}} \qquad \ldots(13)$$

$\theta_{o\,max}$ should converge to the value of θ_o given by equation (2) as B becomes large and reactant consumption can be neglected. When $B \to \infty$, equation (13) gives

$$\theta_{o\,max} = \frac{1}{a} = \frac{\delta p}{\beta'} = \frac{\delta}{\beta'}(1 + \theta'_o) \approx \frac{\delta}{\beta'} e^{\theta'_o} \qquad \ldots(14)$$

Here, $\theta_{o\,max}$ becomes the steady state temperature increase obtained by putting $B = \infty$, $\tau = \infty$ in equation (11).

Identifying θ'_o with $\theta_{o\,max}$, the effective heat transfer coefficient, β, can be evaluated by comparing equation (14) with equation (2) (which does not involve approximation of the conduction term[4]). We then have

$$\beta = \frac{\beta'}{(j + 1)} = \frac{2\alpha}{2 + \alpha} \qquad \ldots(15)$$

Using equation (14) to define a, and treating this as constant, $\theta_{o\,max}$ has been calculated as a function of B from equation (13) and is shown in Fig.1 for $\theta_{o\,max} = 0.2$ at $B = \infty$ (this corresponds to a temperature increase of about $5^{\circ}C$ for some realistic values of E and T_A, equation (3)). The value of δ is 0.98.

It can be shown by differentiation of equation (13) that the relative error in $\theta_{o\,max}$ due to a possible relative error, $\Delta\theta'_o/\theta'_o$, in θ'_o arising from the assumption that θ'_o is constant for all values of B, is of the order $-(\theta'_o)^2 \Delta\theta'_o/\theta'_o$ for $Ba \gg 1$. For the example plotted in Fig.1, it is of the order $-0.04\,\Delta\theta'_o/\theta'_o$ and may be neglected.

The corresponding relationship for τ_m, the time to the maximum temperature increase, is shown in Fig.2. This involves explicit evaluation of β' (see equation (12)); curves are shown for $\alpha = \infty$ and $\alpha = 1$. The lower value of α necessarily implies a lower value of δ for $\theta_o' = 0.2$, namely $\delta = 0.33$. The fraction of reactant consumed in reaching the maximum temperature, calculated by inserting τ_m into the integrated rate equation, is shown in Fig.3; it is independent of α.

For a second order reaction (n = 2), integration of equation (7) and substitution into equation (6) gives

$$\frac{d\theta}{d\tau} = p\delta\left(1 + \frac{p\delta}{B}\tau\right)^{-2} - \beta'\theta_o \qquad \ldots(16)$$

This equation has a solution in terms of the exponential integral but the maximum value of θ cannot be located without considerable computation. Therefore, this has been done by direct integration of the equation on a desk electronic calculator using a Runge - Kutta procedure with an integration interval of 0.01 (a check with an interval of 0.005 confirmed that 0.01 was generally adequate), $\theta_{o\,max}$ being located from the results by inspection. $\theta_{o\,max}$ for the second order reaction, obtained in this way, is plotted in Fig.1 for the same value of $p\delta/\beta'$ as for the first order reaction.

Putting $d\theta_o/d\tau = 0$ in equation (16) and rearranging, the loci of maxima of θ_o are given by

$$\frac{p\delta}{\beta'}\theta_{o\,max} = \left(\frac{\beta'}{p\delta} + \frac{\beta'\tau}{B}\right)^{-2} \qquad \ldots(17)$$

Here, as for the first order reaction, the group $p\delta/\beta'$ is taken as constant (c.f. equation (14)) and is independent of α. Since, from equation (17) $(p\delta/\beta')\theta_{o\,max}$ is defined by the product $\beta'\tau$ for any given value of B, it follows that $\theta_{o\,max}$ (B) is independent of α but that the corresponding values of τ, τ_m, will depend on α (c.f. equation (15)) - as in the case of the first order reaction. Values of τ_m for the second order reaction, identified by inspection from the numerical integration of equation (16) for $\alpha = \infty$, have been plotted in Fig.2 for $\alpha = \infty$ and $\alpha = 1$ using equation (17). The reactant consumption is shown in Fig.3.

A further reaction type of common interest is a first order autocatalytic reaction for which the rate may be expressed in the form

$$\frac{dw}{dt} = k(w_o + w)(1 - w), \quad w_o \ll 1 = \text{constant} \qquad \ldots(18)$$

For this type, it may be concluded from the quasi-stationary model of Merzhanov and Dubovitskii[13] that the maximum temperature rise in sub-critical self-heating will always be close to the value expected for the maximum rate (given approximately by $k/4$). Any discrepancy must be less than that for a simple first order reaction.

DISCUSSION

Effective orders of reaction in the range 0 to 2 may be expected to cover a wide range of practical cases of self-heating in solids. In this range, the effect of reactant consumption on the maximum temperature increase in bodies at ambient temperatures considerably below critical values is relatively small. For example, the results in Fig.1 show that, for a first order reaction, the temperature maximum in a sphere, at an ambient temperature corresponding to $\delta \approx 1$, is only 10 per cent below the value expected for a zero order reaction ($B = \infty$) when B is as low as 8. At this value of B, the "critical" value of δ for thermal explosion in a sphere is about 2.7 times the value expected for a zero order reaction, i.e. about 9. For a reaction doubling in rate for a temperature increase of $10^{\circ}C$, the value $\delta = 1$, thus corresponds to an ambient temperature about $30^{\circ}C$ below "critical". At this level of B, the temperature maximum for a second order reaction is about 15 per cent below the value expected for a zero order reaction.

At values of B as low as 8, however, "critical", or sharply defined, explosion behaviour does not occur. For this[3], B has to be greater than about 14. Even at this level, ignition is not, theoretically really sharply defined[3] although, in practice, it may be sufficiently so[4]. At these higher levels of B it may be concluded that sub-critical self-heating behaviour and critical ignition behaviour will be reasonably consistent on the basis of a model which ignores reactant consumption. It may then be found that estimates of rates of heat generation based on self-heating data are up to about twice the estimates from critical ignition data. Where much larger discrepancies are encountered, an explanation other than neglect of reactant consumption must be sought, e.g. the presence of subsidiary exothermic reactions[4].

The amount of reactant consumed in attaining these small maximum temperatures is small. Explicitly, at a value of δ giving a maximum temperature increase, $\theta_{o\ max}$, of 0.2 when $B = \infty$, the reactant consumption does not exceed 10 per cent until B is below 7 for a first order reaction and below 5 for a second order reaction.

REFERENCES

1. GRAY, P. and LEE, P.R., Combustion and Flame 1965, 9, 202 - 3.
2. BARZYKIN, V. V., GONTKOVSKAYA, V.T., MERZHANOV, A.G. and KHUDYAEV,S.I. Zh. Prik. Mekh. i. Tekh Fiz., 1964, 3, 118 - 125.
3. TYLER, B. J. and WESLEY, T. A. B. Eleventh Symposium (International) on Combustion. pp1115 - 22. The Combustion Institute 1967.
4. THOMAS, P. H. and BOWES, P. C. Brit. J. Appl. Phys., 1961, 12 222 - 9.
5. WALKER, I. K. and HARRISON, W.J. J. Appl. Chem., 1960, 10, 266-76.
6. WAKE, G. C., and WALKER, I. K. New Zealand J. Sci., 1964, 7, 227-41.
7. BENSON, S. W., J. Chem. Phys., 1954, 22, 46 - 50.
8. WILSON, D.J., J. Phys. Chem., 1958, 62 653-5.
9. MORTIMER, R. G., J. Phys. Chem., 1963, 67, 1938 - 9.
10. CHAMBRÉ, P. L. J. Chem. Phys., 1952, 20, 1795 - 7.
11. FRANK-KAMENETSKII, D. A., "Diffusion and heat exchange in chemical kinetics. Translated N. Thon. Princeton University Press, Princeton 1955.
12. THOMAS, P. H. Trans. Faraday Soc., 1960 56 833-9.
13. MERZHANOV, A. G. and DUBOVITSKII, F. I. Reps. Acad. Sci., USSR, 1959, 120 427 - 30.

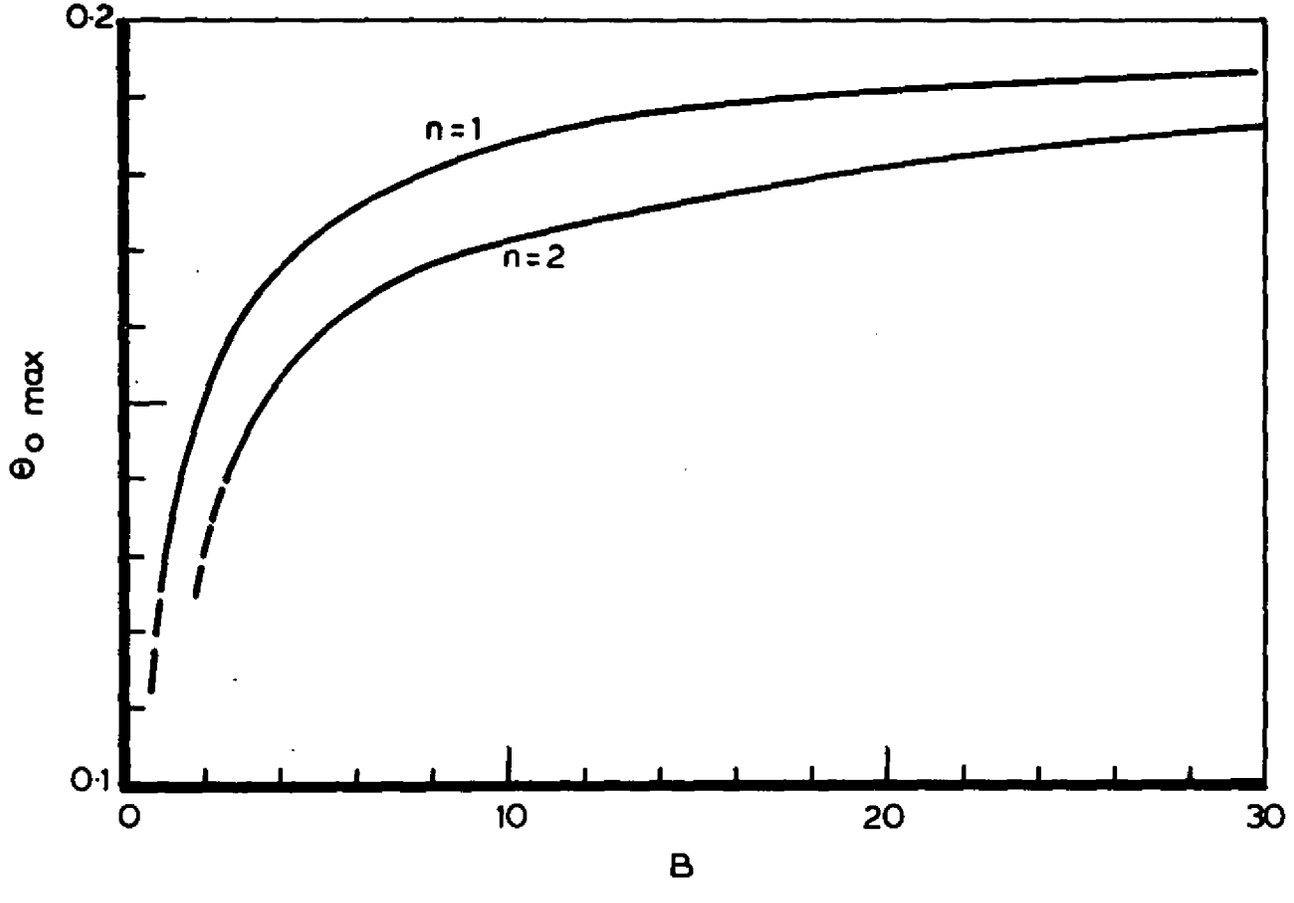

FIG. 1. MAXIMUM SUB CRITICAL TEMPERATURE RISE IN SPHERE

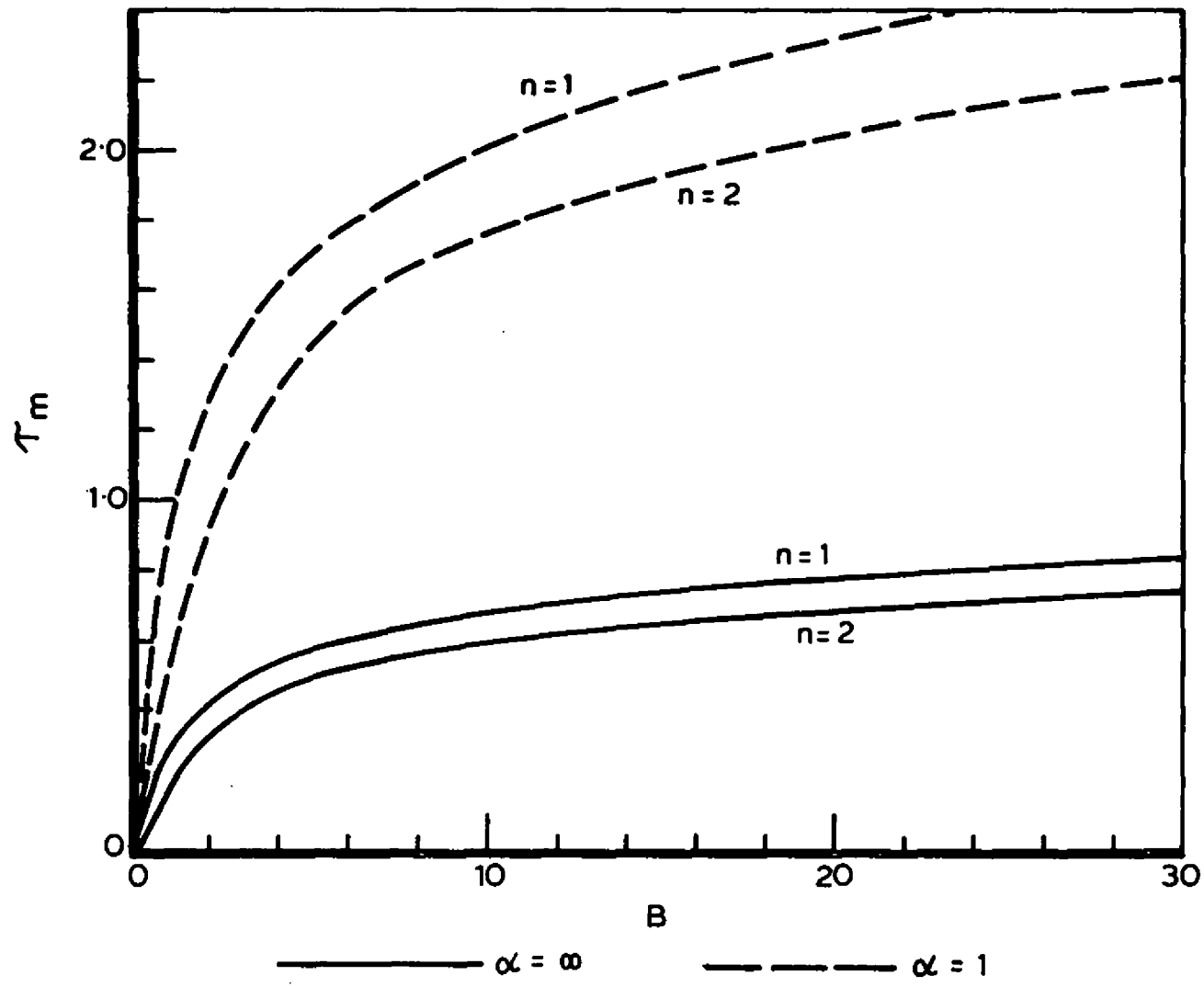

FIG. 2. TIME TO MAXIMUM TEMPERATURE IN SPHERE

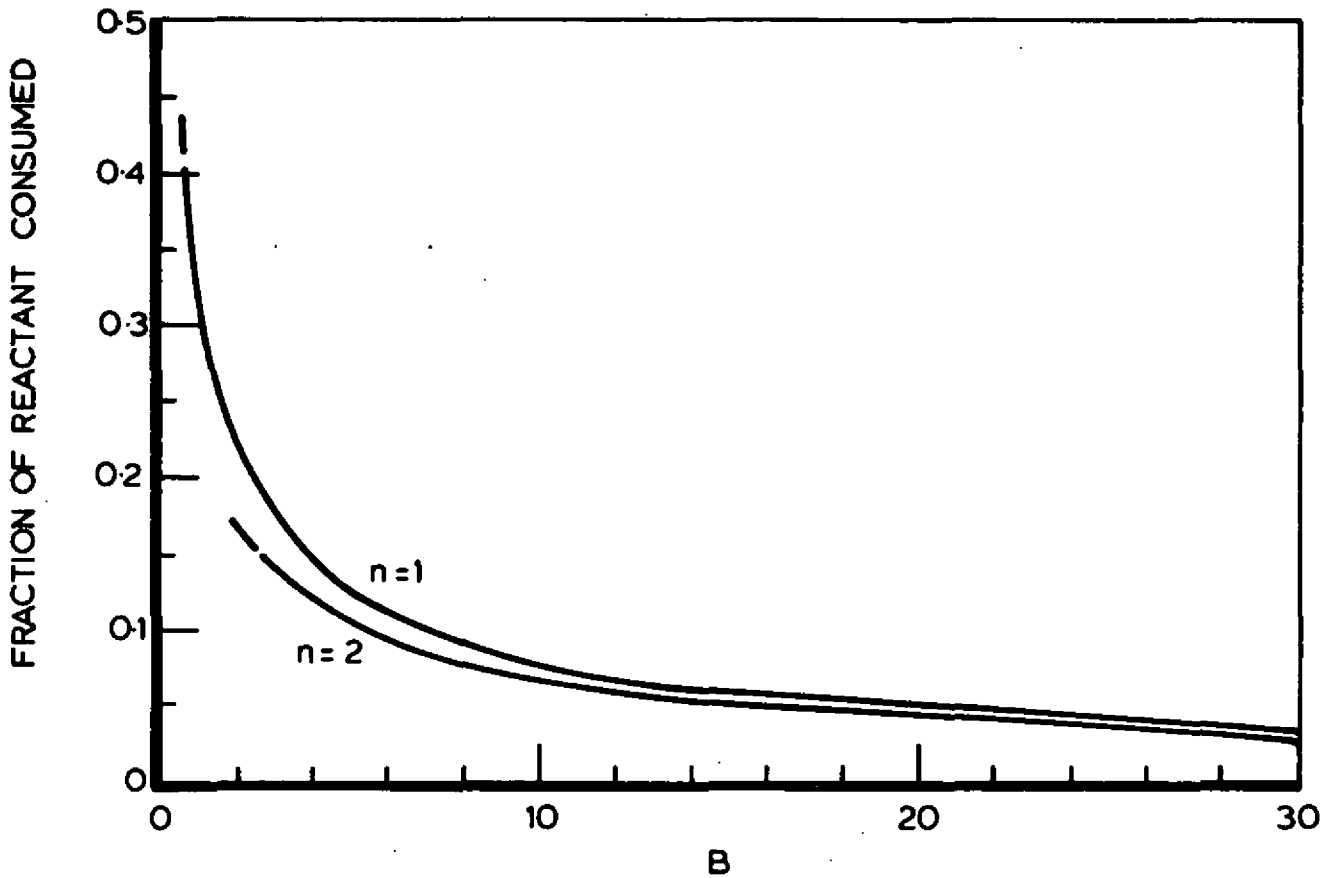

FIG. 3. REACTANT CONSUMED IN REACHING MAXIMUM TEMPERATURE