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Theory of the Burning of Mono-Propellant Droplets

By

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Imperial College, London

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ERRATA

Page 3, line 1, Change \dot{m}''_o to \dot{m}''_c

" line 22, Change \dot{m}'' to \dot{m}''_s

Page 3, line 23, Change 6 to 5

Page 4, line 17,

$$\text{Change } \frac{\sqrt{1 + \frac{4}{A_o}} - 1}{\sqrt{1 + \frac{4}{A_o}} + 1} \quad \text{to} \quad \frac{\left(\sqrt{1 + \frac{4}{A_o}}\right) - 1}{\left(\sqrt{1 + \frac{4}{A_o}}\right) + 1}$$

Page 6, lines 9 and 10 Delete the words "the values of \dot{m}''_f , etc., having been taken uncritically from Reference 3."

Page 6, line 34, Change Ref.4 to Ref.3.

" line 39, Change 5 to 4.

Page 7 line 24, Change 5 to 4

" line 38, Change 4 to 3

Page 8, line 6, Delete line 6

" line 7, Change 4 to 3

" line 8, Change 5 to 4

" line 10, Change 6 to 5

" line 2, Delete the words "mentioned in Ref.3"

Theory of the Burning of Mono-Propellant Droplets

- By -

D. B. Spalding and V. K. Jain,
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19th May, 1958

SUMMARY

Formulae are derived for the burning rate and time of mono-propellant droplets suspended in an atmosphere of their own decomposition products. The liquid temperature is assumed constant and the activation energy of the reaction is supposed high. Some experimental data are cited in qualitative support of the theory.

1. Introduction

1.1 Purpose of paper

The theory of the burning rate of liquid-fuel droplets in an oxidising medium is well understood, and well supported by experiment. A particular feature of such processes is that their rate is scarcely influenced by the rate constants of the chemical reaction.

When the liquid is chemically unstable on the other hand, i.e., when it is a mono-propellant, the rate of decomposition of the vapours affects the rate of vaporization. It is this influence which is examined in the present paper, the aim of which is to provide formulae from which the burning rates and burning times can be calculated.

1.2 Treatment

The case considered is the relatively simple one in which:-

- (a) the droplet temperature is constant
- (b) the flame is spherically symmetrical
- (c) the gaseous atmosphere surrounding the droplet consists of the products of adiabatic combustion of the liquid.

In addition, it is assumed that the activation energy of the chemical reaction is so high that the thickness of the flame may be taken as very small compared with its curvature. In this respect the treatment is essentially that of Adams¹.

1.3 Main results

Qualitatively, it appears that the effect of the chemical reaction is always to increase the burning rate and reduce the burning time of the mono-propellant droplet as compared with a chemically stable droplet with the same physical properties.

This/

This effect decreases however as the size of the droplet decreases. Very small droplets vaporize at a rate which is uninfluenced by the chemical reaction.

Explicit formulae are derived below for the burning rate and burning time. It is shown that, in addition to the usual physical constants, it is also necessary to know the speed of propagation through the vapour of a plane laminar flame. Each of the formulae takes the form of a relation between two dimensionless groups, one containing only physical quantities, the other containing the flame speed as well.

The formulae in question are equations (8) and (11) below. They are represented graphically in Figs. 2 and 3.

1.4 Relevance to one-dimensional rocket theory

In an accompanying paper², the law of droplet vaporization is needed for the determination of the L^* of a rocket. This law enters the theory in the form of a function, β , of droplet radius. The present paper provides such β functions. Some are plotted in Fig. 4.

2. Theory

2.1 The problem

Consider the droplet, of radius r_g , and concentric flame, of radius r_f , shown in Fig. 1a. The temperature distribution along a radius will have the general shape shown in Fig. 1b, characterized by a uniform value within the liquid phase, a rising value between the liquid surface and the flame, and a uniform value outside the flame.

Consistently with the assumption of high activation energy, the flame has been drawn as a thin spherical surface at which the temperature gradient exhibits a discontinuity; it is this consequence of the assumption which permits the following simple analysis.

As a result of heat conduction to the surface, liquid fuel vaporizes. The vapour streams radially outwards, eventually reaching the flame. Here chemical reaction takes place with a release of energy; the fuel is consumed and combustion products at the adiabatic combustion temperature flow outward into, and indeed constitute, the surrounding reservoir of gas.

The task is to calculate the rate of vaporization and so the burning time of the droplet. To do this we have to take account of the following considerations:-

- (a) The surface vaporization rate is proportional to the gas temperature gradient there;
- (b) The flame adjusts itself so that the rate of fuel flow through it, per unit area, is equal to the laminar flame speed, assumed known.
- (c) The intermediate region obeys the Fourier conduction law and the steady-flow energy equation.

2.2 Differential equation and boundary condition

If the mass rate of flow of vapour through unit area of the spherical shell of radius r is \dot{m} , the gas conductivity is k , the fuel vapour specific heat at constant pressure is c and is assumed constant, and the gas temperature is T , the steady-flow energy equation applied to a control volume bounded by spheres of radius r and $r + dr$, yields:

$$\frac{1}{r^2}$$

$$\frac{1}{r^2} \frac{d}{dr} \left(k \frac{dT}{dr} \right) - \dot{m}'' \frac{dT}{dr} = 0. \quad \dots(1)$$

The conservation-of-mass principle, applied to the spherical surfaces of radius r , r_s and r_f , yields

$$\dot{m}'' r^2 = \dot{m}''_s r_s^2 = \dot{m}''_f r_f^2 \quad \dots(2)$$

where \dot{m}''_s is the surface vaporization rate which it is desired to find, and \dot{m}''_f is the mass burning rate in the flame which is supposed given ($\dot{m}''_f = \rho_u S_u$ in usual notation where ρ_u = density of unburned material, S_u = flame speed relative to unburned material).

The boundary conditions are:-

$$r = r_s : \quad T = T_s \quad \dots(3)$$

$$\dot{m}''_s Q = (k \frac{dT}{dr})_s \quad \dots(4)$$

$$r = r_f : \quad T = T_f \quad \dots(5)$$

where Q = heat transfer to liquid from gas per unit mass transfer; Q is supposed to be equal, in this case, to the latent heat of vaporization of the propellant.

2.3 Solution for burning rate

Integration of (1), and substitution from (2), (3) and (4), yields the following results:

$$\dot{m}''_s r_s (1 - r_s/r_f) = \int_{T_s}^{T_f} \frac{k dT}{c(T - T_s) + Q} \quad \dots(6)$$

For comparison with a familiar result for constant-property mass transfer, we write this as

$$\frac{\dot{m}''_s r_s}{\bar{k}/c} (1 - r_s/r_f) = \ln(1 + B) \quad \dots(7)$$

where $B = c(T_f - T_s)/Q$, the transfer number for vaporization⁶,

\bar{k} = a mean thermal conductivity, defined as:-

$$\bar{k} = c \int_{T_s}^{T_f} \frac{k dT}{cT + Q} / \ln(1 + B).$$

r_f can be eliminated by introducing \dot{m}''_f from (2). After some algebra, we obtain

$$\frac{\dot{m}''_s r_s}{(\bar{k}/c) \ln(1 + B)} = \frac{2}{2 + A - \sqrt{A^2 + 4A}} \quad \dots(8)$$

where $A \equiv \frac{\dot{m}''_f r_s}{(\bar{k}/c) \ln(1 + B)}, \quad \dots(9)$

Equation (8) is plotted in Fig. 2. It will be seen that at $A = 0$ (unreactive vapour) the ordinate equals unity, while as $A \rightarrow \infty$ (very reactive vapour) the ordinate tends to A , i.e., $\dot{m}_s'' \rightarrow \dot{m}_f''$.

2.4 Solution for burning time

Equation (8) holds strictly for the steady state. In reality r_s decreases with time in accordance with

$$\frac{dr_s}{dt} = - \frac{\dot{m}_s''}{\rho_\ell} \quad \dots(10)$$

where t = time, and

ρ_ℓ = density of droplet.

Provided that this rate is small compared with the rate of adjustment of gas conditions to changes in flow rate, equation (8) can be used for the varying-radius case also. We do this here.

Since r_s appears on both sides of equation (8), some rearrangement is needed before, with the help of (10), it becomes an integrable equation with r_s the dependent and t the independent variables. Integration then yields

$$\frac{t_b (\bar{k}/c) \ln(1+B)}{\rho_\ell r_{s_0}^2} = \frac{1}{2} + \frac{A_0}{6} + \frac{2}{A_0^2} \ln \left[\frac{\sqrt{1 + \frac{4}{A_0} - 1}}{\sqrt{1 + \frac{4}{A_0} + 1}} \right] + \sqrt{1 + \frac{4}{A_0}} \left[\frac{1}{A_0} - \frac{1}{6} - \frac{A_0}{6} \right] \quad \dots(11)$$

where t_b is the time during which the droplet changes from

r_{s_0} , its initial radius, to zero radius, and

A_0 = value of A where $r_s = r_{s_0}$.

Equation (11) is represented graphically in Fig. 3. When $A_0 = 0$ (unreactive fuel, small droplet), the ordinate is equal to $1/2$, which is a well-known result; as A_0 increases, the burning time decreases.

2.5 Solutions in a form suitable for one-dimensional rocket theory

In a theory of liquid-fuel rocket combustion presented elsewhere (Ref. 2), it is necessary to determine how the burning rate varies with droplet radius. Introducing the symbols:-

for radius, $\zeta \equiv r_s/r_{s_0} \quad \dots(12)$

and

for burning rate, $\beta \equiv \dot{m}_s''/\dot{m}_{s_0}'' \quad \dots(13)$

the required relation between β and ζ is derived by re-arranging (8). It is

$$\beta = \frac{1}{\zeta} \frac{2 + A_0 - \sqrt{A_0^2 + 4A_0}}{2 + A_0\zeta - \sqrt{A_0^2\zeta^2 + 4A_0\zeta}} \quad \dots (14)$$

Curves of β versus ζ are plotted from equation (14) in Fig. 4. When $A_0 = 0$, we have $\beta = 1/\zeta$ as for pure vaporization. For larger values of A_0 (more reactive fuels) β increases less rapidly as ζ , the droplet radius, falls to zero. For $A_0 = \infty$, $\beta = 1$.

3. Discussion

3.1 The rôle of chemical reaction

(a) Influence on burning rate

Fig. 2 shows that the occurrence of chemical reaction always acts so as to increase that for pure vaporization, the rate of increase with A being greatest for small values of A . At large values of the chemical rate parameter A , the transfer number B is without influence on the vaporization rate; chemical reaction rate is controlling. This behaviour of mono-propellant droplets is in strong contrast to that of bi-propellant systems (e.g., hydrocarbon fuel droplets in an oxidising atmosphere); for these are only influenced by chemical reaction rate when this is low.

A consequence is that, since for most mono-propellants the flame speed m_f'' is approximately proportional to absolute pressure, whereas B is relatively insensitive to pressure, an increase of pressure increases the rate of vaporization; an increase of pressure tends to make chemical reaction controlling.

A practical conclusion is that the L^* of mono-propellant rockets can be decreased by an increase of operating pressure. If the same advantage is desired for a bi-fuel rocket, it must be contrived that fuel and oxidant are pre-mixed in the liquid phase so as to be both present within a single droplet.

It should be noted that A has a clear physical significance. It is the ratio of the mass burning rate of fuel in a plane laminar flame, to the mass rate of vaporization at the droplet surface if chemical reaction is absent.

(b) Influence on burning time

Fig. 3 shows how chemical reaction reduces the burning time. The reduction is considerable, even for small values of A_0 . Thus if $A_0 = 1$, the burning time is about one half that for zero chemical reaction.

Of course, every mono-propellant droplet, as it nears the end of its life, passes into a régime in which only physical processes control; for A tends to zero as r_s tends to zero.

(c) Influence on one-dimensional rocket theory

Solutions of the one-dimensional rocket equations using the β - ζ curves of Fig. 4 will be reported elsewhere. It is clear however that, since β is lower for large A_0 than for small, the non-dimensional characteristic length, ξ^* , of Ref. 2 will be larger for large A_0 than for $A_0 = 0$.

This does not of course mean that the L^* of the reactive fuel is greater than that of the unreactive, but arises simply from the way in which ξ^* has been defined in terms of the initial vaporization rate of the droplet. We should in fact compare ξ^* for the unreactive fuel with $\xi^* \times (k/c) \ln(1+B)/m_{s0}'' r_{s0}$ for the reactive one. It will always appear that an increase in A_0 tends to decrease L^* .

3.2 Actual values of A

Tables 1 and 2 show values of B and A/r_s for four different liquid mono-propellants, the values for m_p'' , etc., having been taken uncritically from Ref. 3. It may be seen that B decreases slightly as the pressure rises; this is because of the rise in boiling point. A/r_s rises partly on this account, but more because of increase of m_p'' with pressure.

The initial radius for a mono-propellant droplet entering a rocket is of the order $r_{s0} = 5 \times 10^{-3}$ cm. Thus the value of A_0 for ethyl nitrate would be 5 at 60 atm, and 0.078 at 1 atm. For nitro methane, to go to the other extreme, the respective values are 1.6 and 0.022.

If, in a bi-propellant rocket, accident or design cause fuel and oxidiser to be simultaneously present in a single droplet, values of A_0 an order of magnitude greater than those of Table 2 may be expected. The reason is that the laminar flame speeds of such mixtures are very much greater than those of practical mono-propellants; for the latter must be sufficiently insensitive to be handled with safety, a requirement that normally precludes a high flame temperature.

Inspection of Fig. 3, for example, reveals that the A_0 values just calculated entail an appreciable reduction in the time of burning. This is bound to be reflected in the minimum L^* of the rocket. We may also deduce that an increase of chamber pressure will reduce the minimum L^* and that, for example, propyl nitrate will require a longer chamber than ethyl nitrate. The latter result is as much a consequence of the low B of propyl nitrate as of its low A/r_s .

Experimental results obtained with small rocket motors are available (Ref. 4), which bear out the above predictions qualitatively. However a closer examination of the theory and experimental data is needed.

3.3 Experimental data on mono-propellant droplet combustion

No experimental data are known to the authors on mono-propellant droplet vaporization in an atmosphere of droplet combustion products. Barrère and Moutet⁵ have measured burning times for various mono-propellant droplets in a heated nitrogen or air atmosphere. The influence of the "foreign" atmosphere prevents quantitative comparison with the present theory. However the following points may be noted:-

(i) Within the experimental accuracy, and with fixed atmospheric conditions, the burning rate per unit area was proportional to the reciprocal of the radius. This is not quite the result expected from the above theory; however the expected deviations would be only small, and the accuracy of the experiments would scarcely permit their detection.

(ii) The occurrence of the decomposition reaction definitely increased the vaporization rate. This was made evident by, for example, a sharp change in the rate of vaporization of hydrogen peroxide droplets consequent on a small rise in nitrogen temperature. The rate of increase was too sharp to be accounted for other than chemically.

(iii)/

(iii) The composition and temperature of the surrounding atmosphere were influential. A temperature effect has just been mentioned. A composition effect was the increased rate produced by replacing nitrogen by air of the same temperature when the mono-propellant vapour was oxidisable.

3.4 Further work

The present paper represents only the first step in analysing liquid mono-propellant combustion theoretically. The following further steps need to be taken:-

(a) Developments in theory

- (i) Use of β - ζ curves of Fig. 4 in one-dimensional rocket theory in order to calculate L^* , etc.
- (ii) Examination of the theory of spherical flames which are not thin compared with their radius of curvature. Such an examination will eliminate the error associated with the above thin-flame assumption, but will inevitably involve more complicated burning rate relations.
- (iii) Investigation of the case in which the liquid is injected cold and heats up simultaneously with vaporization and combustion.
- (iv) Investigation of the case in which the atmosphere consists, not of propellant decomposition products, but of a gas capable of chemical reaction with these products. This is the case of Ref. 5, and must often be of importance in rockets.

The above problems are under investigation in the authors' laboratory.

(b) Experimental

- (i) The technique of Barrère and Moutet should be applied to droplets in an atmosphere of decomposition products.
- (ii) Techniques which have been developed for stable fuels, such as the burning of liquid propellants from artificial surfaces in controlled gas streams, could also be used with advantage. However the danger of explosion renders it impractical to carry out this work in a university.
- (iii) More work on the influence of fuel, pressure and L^* on mono-propellant rocket motor efficiency is needed. The data mentioned above (Ref. 4) form a useful beginning.

(c) Data collection and analysis

- (i) Propellant data (heats of reaction and vaporization, specific heats, vapour pressures, and flame speeds) are scanty and, in some cases doubtful. A thorough review and augmentation of the data are needed.
- (ii) With these data, and the theories of the present paper and of Ref. 2, comparisons between experimental and predicted rocket performance can be made. Such comparisons appear to offer the best chance of developing rocket motors other than by trial-and-error.

References

1. G. K. Adams - Unpublished work.
 2. D. B. Spalding - "A one-dimensional theory of liquid-fuel rocket combustion". C.P.445. May, 1958.
 3. Deleted.
 4. G. K. Adams - Private communication.
 5. M. Barrère and H. Moutet - Recherche Aeronautique, March-April, 1956, No.50, p.31.
 6. D. B. Spalding - "Fourth Symposium on Combustion", Williams and Wilkins, Baltimore, p.847.
-

TABLE 1/

TABLE 1

Transfer Numbers, B, of liquid mono-propellants

Pressure	Ethyl nitrate	Propyl nitrate	Hydrazine	Nitromethane
1 atm	6.73	1.86	2.63	5.56
10 "	5.50	1.52	2.29	4.64
20 "	5.06	1.51	2.20	4.36
40 "	4.80	1.42	2.08	4.03
60 "	4.49	1.37	2.01	3.88

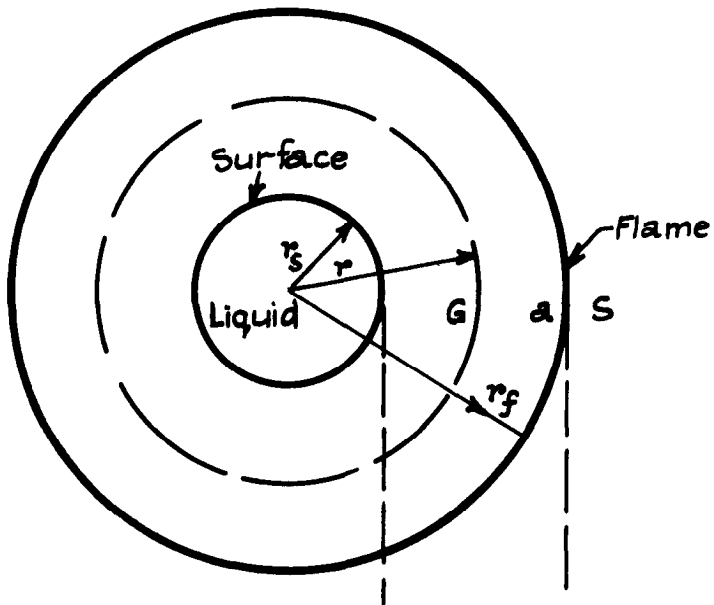
TABLE 2

A/r_s , in cm^{-1} , for liquid mono-propellant droplets

Pressure	Ethyl nitrate	Propyl nitrate	Hydrazine	Nitromethane
1 atm	15.6	9.5	85.3	4.4
10 "	170.9	124.5	295.9	48.2
20 "	355.2	250.0	421.3	99.3
40 "	866.8	520.4	617.8	206.4
60 "	1010.0	799.5	771.3	315.5

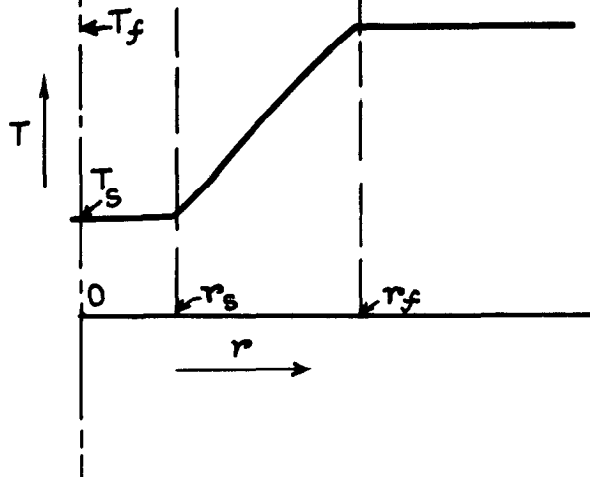
FIG. 1a & 1b.

FIG. 1a.



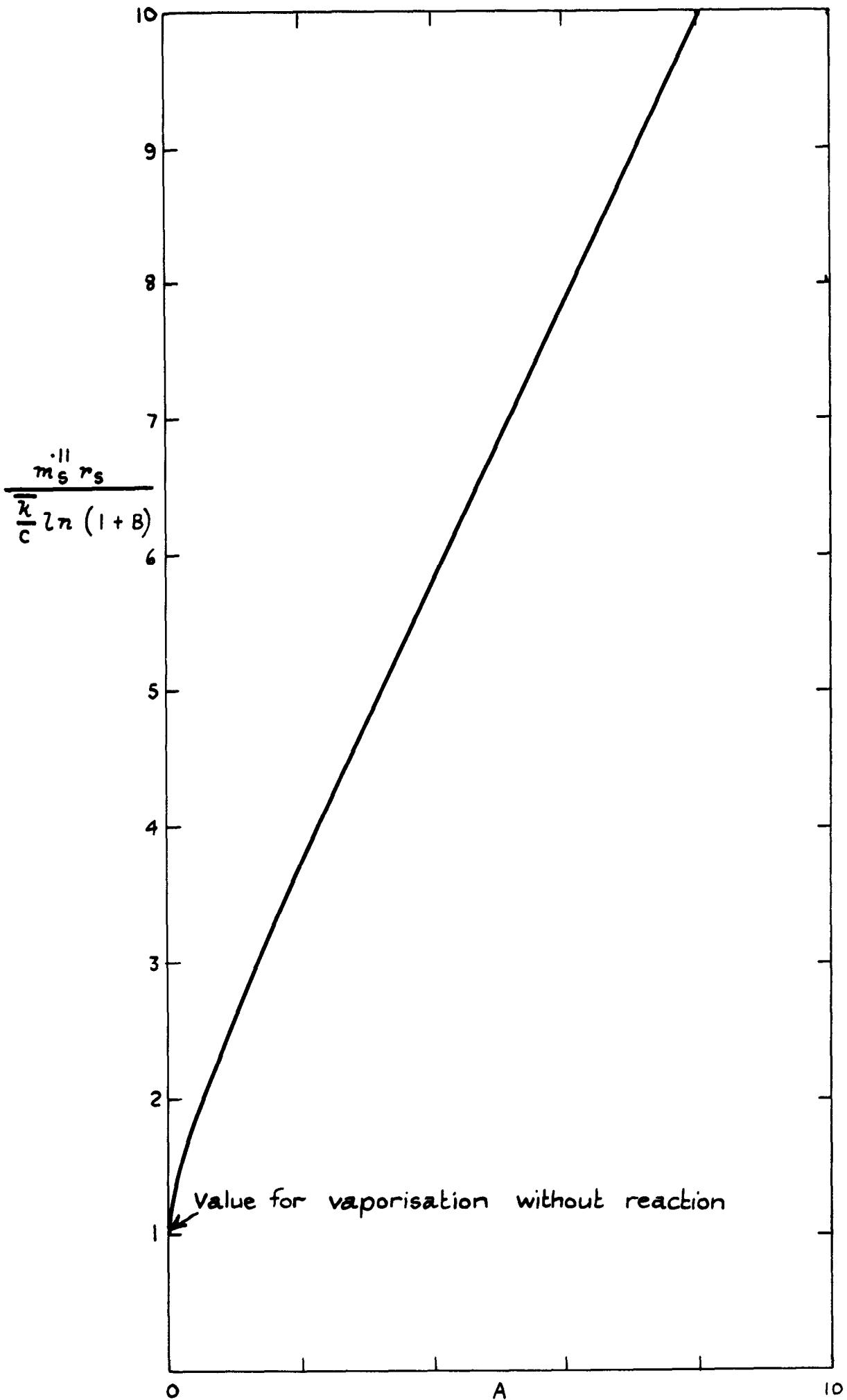
Burning monopropellant droplet.

FIG. 1b.



Temperature distribution adjacent droplet.

FIG. 2.



Variation of $\frac{m_s r_s}{\frac{k}{c} \ln(1+B)}$ with A.

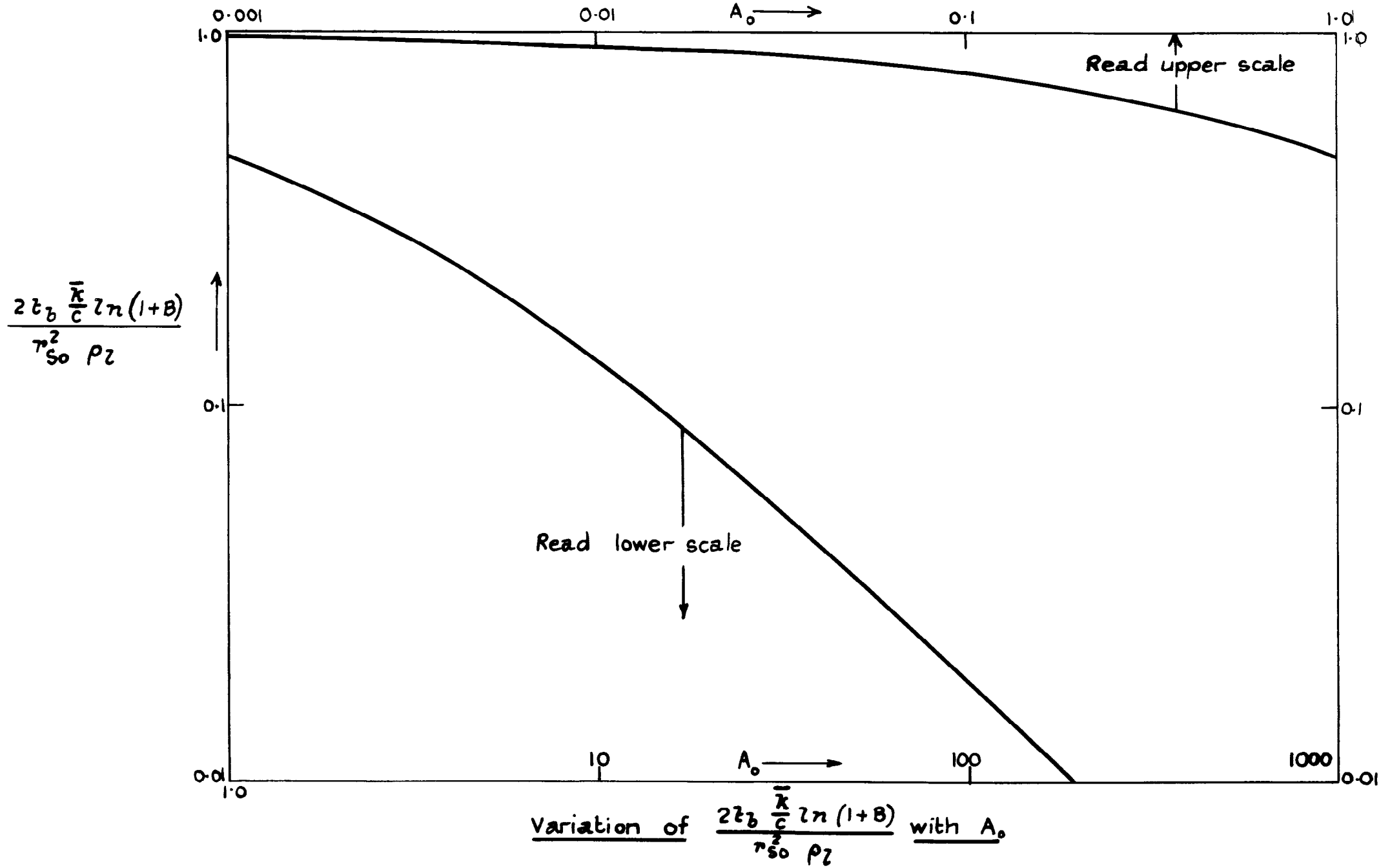
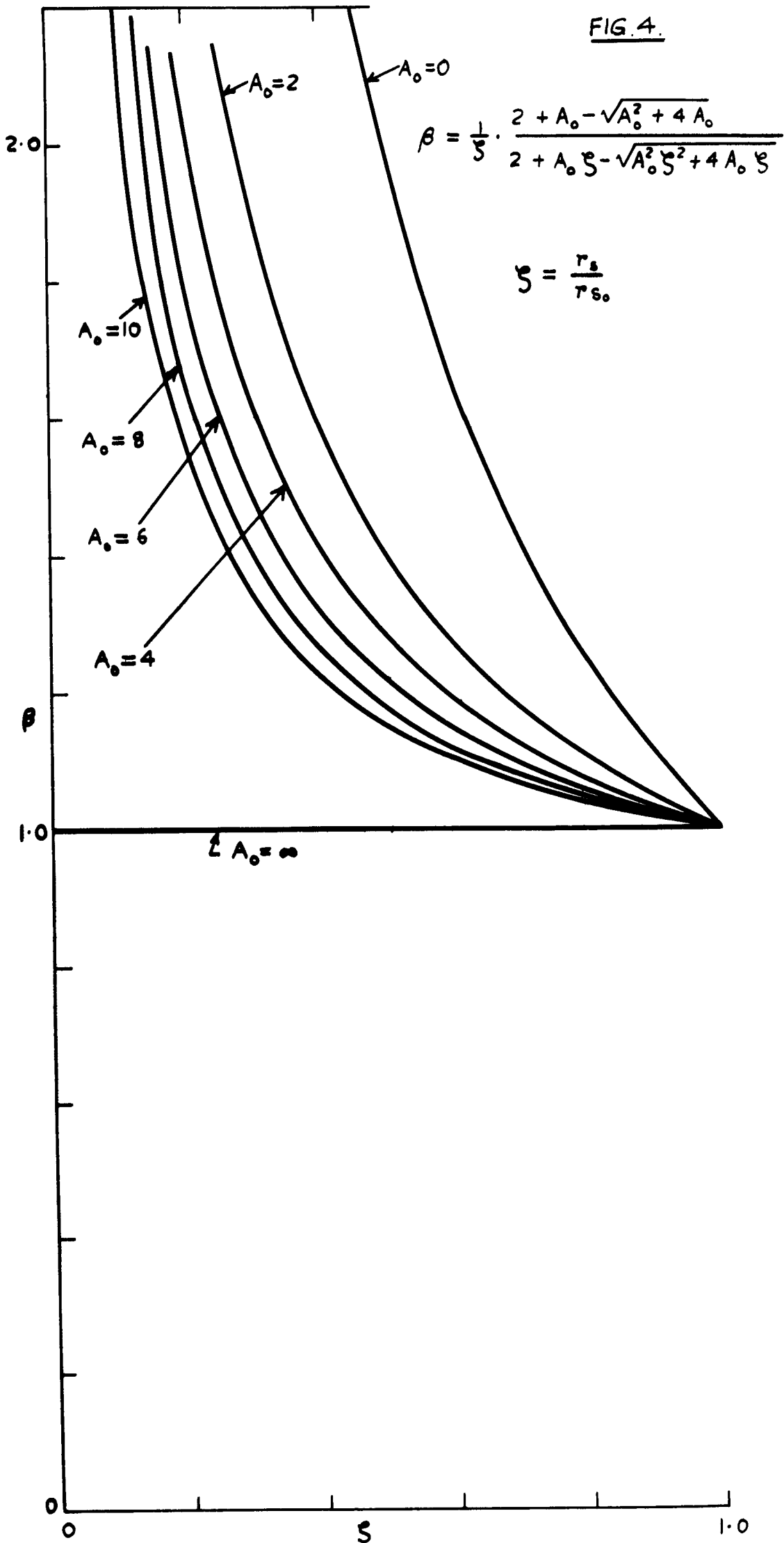


FIG. 3.

FIG. 4.



Variation of β with ζ .

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