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ON THE ROLE OF DIFFUSION OF OXYGEN IN THE SELF IGNITION OF  
FIBRE INSULATING BOARD AND WOOD

by

P. H. Thomas

Summary

The self-heating equation is derived in an approximate form for simultaneous thermal and mass diffusion in a symmetrically heated porous solid. This equation has already been discussed by Buben (1) and its application to the self ignition of fibre insulating board and wood is described here. Some of the numerical values of the relevant parameters are derived for fibre insulating board and wood and they show that fibre insulating board is sufficiently porous for there to be a sharp ignition point thermally controlled. The critical ignition parameters for fibre insulating board, and dust piles which are more porous but equally reactive and exothermic are theoretically little affected by whether or not the reaction is oxygen dependent. If the reaction requires oxygen there is a temperature jump to a region where oxygen availability controls the reaction. Calculated values are obtained from the theory for the temperature jump on the assumption that there is no exhaustion of reactant in the solid frame.

October 1959

Fire Research Station,  
Boreham Wood,  
HERTS.

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1. Introduction

The problem to be discussed is the relative importance of the diffusion of heat and oxygen in the self-heating and ignition of fibre insulating board and wood. In the absence of definite information as to the role of oxygen in self-heating this paper explores some of the consequences of the assumption that the heat generation in self-heating is oxygen dependent. Only qualitative conclusions can be drawn at present but it can be shown that with certain simplifying assumptions an equation can be derived which has been discussed already by Buben (1) and which demonstrates certain well known features of the ignition of various combustible solids. We assume (a) that within any elementary volume the temperatures of the solid and the gases in the pores within the solid are the same, (b) that the reaction is zero-order with respect to the solid, and of order "m" with respect to oxygen and (c) that it obeys the Arrhenius Law. We shall discuss here only the case of symmetrical heating.

We write:-

- r the half thickness of a slab or radius of the cylinder or sphere
- T absolute temperature
- E activation energy
- R the universal gas constant
- x the distance from the centre of the slab, cylinder or sphere
- Q the heat of reaction per unit volume of oxygen at N.T.P.
- m rate of consumption of oxygen, mass per unit volume of gas phase per sec.
- ε the porosity of the solid
- s surface per unit volume
- f a pre-exponential factor of dimensions length/time
- ρ is the density of oxygen
- K the thermal conductivity of the material
- D the gaseous diffusion coefficient
- w the concentration of oxygen by volume of gas phase
- ∇ the Laplacian operation  $\frac{\partial^2}{\partial x^2} + \frac{1}{x} \frac{\partial}{\partial x}$  and k is 0, 1 and 2

for the slab, cylinder and sphere respectively.

The heat transfer equation for a symmetrically heated body  
- r  $\lll$  r is thus, for the steady state

$$K \cdot \nabla^2 T = - \frac{Q \epsilon m^{m+1}}{f} \quad \dots \dots (1)$$

The mass diffusion equation is

$$D \nabla^2 w = \frac{\epsilon m^{m+1}}{f} \quad \dots \dots (2)$$

and

$$D = 0.66 D_0 \epsilon \quad \dots \dots (3)$$

a formula given by Penman (2) for the diffusion coefficient of a solid of porosity (in terms of the coefficient  $D_0$  in air. Results given by Dye and Dallaville (3) suggest that this may slightly underestimate  $D$ . The coefficient could not exceed 1.0 so there is at most a 50 per cent error here.

The reaction equation for a reaction of order "m" on the internal surface of the solid, neglecting changes in total pressure, may be written

$$M''' = p.f.w.s. e^{-E/RT} \dots\dots (4)$$

## 2. Theoretical

From equations (1) and (2)

$$K \nabla^2 T + \phi D \nabla^2 w = 0 \dots\dots (5)$$

The boundary conditions are

$$\frac{dT}{dx} = \frac{dw}{dx} = 0 \quad \text{at } x = 0$$

$$T = T_0 \\ w = w_0 \quad \text{at } x = \pm r$$

so that from (5) we have

$$\frac{K}{\phi D} (T - T_0) = w_0 - w$$

Hence

$$\nabla^2 T = - \frac{p.f.E.s.w_0^m e^{-E/RT}}{K} \left( 1 - \frac{K(T - T_0)}{\phi D w_0} \right)^m \dots\dots (6)$$

As an approximation (4) we replace

$$-\nabla^2 T \quad \text{by} \quad - \frac{(1+k) \bar{D}_k (T - T_0)}{r^2} \dots\dots (7)$$

where  $k$  and  $\bar{D}_k$  are respectively 0 and 2.4 for a slab, 1 and 1.7 for a cylinder and 2 and 3.0 for a sphere.

The values of  $\bar{\alpha}_k$  quoted are Frank Kamenetskii's effective transfer coefficients (4) which, although distorting slightly the temperature distribution, are chosen to give the correct value of the critical parameter in the case without mass transfer. Thus

$$\bar{\alpha}_k (1+k)(T-T_0) = \frac{Q f s r^2 \omega_0 e^{-E/RT}}{K} \left(1 - \frac{K(T-T_0)}{Q D \omega_0}\right)^{1/2}$$

which is of the form

$$(T-T_0) = A e^{-E/RT} (1 - B(T-T_0))^{1/2} \quad \dots (8)$$

where

$$A = \frac{Q f \omega_0 r s r^2}{K \bar{\alpha}_k (1+k)} \quad \dots (9)$$

and

$$B = \frac{K}{Q D \omega_0} \quad \dots (10)$$

### 3. Application of theory

#### 3.1. Existence of sharp ignition point

For fibre insulating board

$$K = 1.2 \times 10^{-4} \text{ cal cm}^{-1} \text{ } ^\circ\text{C}^{-1} \text{ s}^{-1}$$

Q is of order 2 cal cm<sup>3</sup> of oxygen (5) - a value obtained for coal and assumed in this problem to be the same for wood. <sup>\*</sup>

$$W_0 = 0.21$$

$$D_0 = 0.18 \text{ cm}^2 \text{ sec}^{-1}$$

$$\epsilon = 0.8$$

Hence

$$B = 0.003$$

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<sup>\*</sup> This is of the same order as the heat released in the oxidation of carbon. For the monoxide it is 2.6 and the dioxide 4.4 calories/cc.

A larger estimate of D would reduce B.

Equation (8) has been studied by Buben (1). The relation between T and  $T_0$  is shown diagrammatically in Fig. 1.

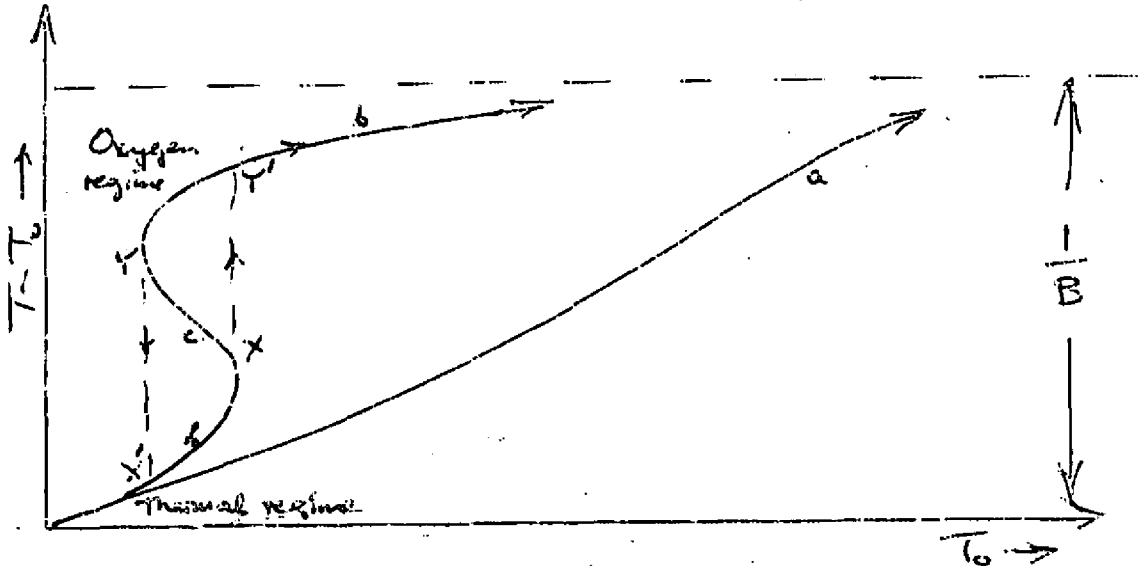


Fig. 1. Characteristic self-heating curve

Buben shows that there is a condition which must be satisfied in the following discussion viz. that  $E/RT_0 > 4$  but for normal values of E and T this is always satisfied. More important, if  $BRT_0/c > 1/4$  there are no critical points (curve (a) in Fig. 1) but if  $BRT_0/c < 1/4$  there are two points (X) and (Y) which divide the steady state equilibrium into three kinds, a thermally controlled regime, an oxygen diffusion controlled regime, and an unstable regime separating the first two. (c) in Fig. 1.

We can illustrate the significance of these as follows. Suppose heating takes place in an oven in which  $T_0$  is raised very slowly so that the material can be regarded as always in equilibrium on curve (b) near the origin. Here it is the thermal balance which is important. As  $T_0$  rises  $T - T_0$  rises and eventually point (X) is reached. Further increase in  $T_0$  must cause a jump to (Y) where in the new equilibrium the predominant role is played by the limitation to the oxygen supply. It is this jump which is the sharp ignition point. In practice, another reaction may become important at the higher temperatures but this would not affect the principle of the argument. The reverse happens on cooling, only the jump is from (Y) to (X). Clearly as B becomes larger the critical points become less well defined.

For fibre insulating board  $E = 25,000$  so that

$$\frac{BRT_0^2}{E} \sim 0.07$$

which is less than 0.25 so that there is a sharply defined critical ignition. It is indeed observed that after ignition in a furnace (6) the rate of rise of temperature of fibre insulating board rises rapidly for a time and then falls until the charring reaches the outside surface - when presumably the oxygen supply can increase rapidly because of the cracking that has occurred in the charcoal.

There are some data for the diffusivity of hydrogen and carbon dioxide in air for different woods (7) both along and across the grain. Across the grain the diffusivities for hydrogen are of order

$$2 \times 10^{-4} \text{ to } 5 \times 10^{-4} \text{ cm}^2/\text{s}$$

Along the grain there is a considerable variation from wood to wood. For Norway spruce, Douglas Fir and quick grown Ash, D has a value of order 0.12 for hydrogen. Since  $D_0$  for hydrogen is 0.61 and for oxygen in air 0.18 we must reduce the above value by this ratio 0.18/0.61 to obtain values for oxygen and we conclude that if the only diffusion is across the grain there can be no sharp ignition points in wood. Even allowing for diffusion along the grain it is doubtful if for the named woods there could be sharp ignition points. However, for Beech, Poplar and slow grown Ash the diffusional flow of gas is 10 - 100 times greater than for Spruce, Douglas Fir and fast grown ash. If an appreciable proportion of the exposed surface were end grain, one might expect a sharp ignition point for these woods.

### 3.2. Critical values of the temperature rise

Buben has discussed these equations for any value of "m". Proceeding in the same way equation (8) may be written

$$A e^{-\frac{1}{y+x}} = \frac{\frac{E}{R} x}{\left(1 - \frac{E\beta}{R} x\right)^m} \quad \dots\dots (11)$$

i.e. where  $y = \frac{RT_0}{E}$  and  $x = \frac{R(T-T_0)}{E}$

Differentiation of equation (11) leads, when  $\frac{dy}{dx}$  is put equal to zero, to

$$\frac{x}{(x+y)^2} = \frac{1 + (m-1) \frac{R\beta T_0^2}{E} \frac{x}{y^2}}{1 - \frac{R\beta T_0^2}{E} \frac{x}{y^2}} \quad \dots\dots (12)$$

Let  $\frac{E(T-T_0)}{R T_0^2} = \frac{x}{y^2} = \theta$

and  $c = \frac{R\beta T_0^2}{E}$

From equation (12) we then have the equation for the critical values

$$\theta_c (1 - c \theta_c) = (1 + \theta_c y)^2 (1 + (m-1) c \theta_c) \quad \dots\dots (13)$$

It can be shown (1) that  $y < \frac{1}{4}$  is a necessary condition - though not a sufficient one for there to be critical values of  $\theta$ . For "m" equal to unity it follows from (13) that the critical values are

$$\theta_c = \frac{1 - 2y \pm \sqrt{1 - 4y - 4c}}{2(c+y)}$$

Now  $4y = \frac{4 \times 2 \times 550}{25,000} \approx 0.18$

i.e. C must be less than 0.20. If y is assumed zero, the critical value of C, as mentioned above equals 0.25.

For values of  $y$  and  $C$  pertaining to fibre insulating board i.e. 0.04 and 0.1 respectively, the critical ignition point  $X$  occurs at  $\theta$  equal to 1.26, a 26 per cent greater temperature rise than would occur if gaseous diffusion were neglected (i.e.  $m = 0$ ). This increase is, however, dependent on the value of "m" but the effect is not large. This can be readily shown to be so for the limiting case  $y = 0$  (for very large activation energies i.e. neglecting  $\theta_y \ll 1$ ). Thus we have from equation (13) with  $y$  zero

$$\theta_c = \frac{1 - (m-1)c \pm \sqrt{[1 - (m-1)c]^2 - 4c}}{2c} \dots\dots (14)$$

the negative sign indicating the ignition point  $X$ . Equation (14) shows that there are only critical values to  $\theta_c$  if  $C$  is less than  $(1 + \sqrt{m})^{-2}$ . For  $c$  equal to  $(1 + \sqrt{m})^{-2}$ , the critical value of  $\theta_c$  is equal to  $1 + \sqrt{m}$ . For  $C = 0.1$ , we obtain values of  $\theta_c$  for various values of  $m$ . These values are given in Table I.

TABLE I

$m$	$\theta_c$ $c = 0.1$	$\theta_c$ $c = (1 + \sqrt{m})^{-2}$
0	1.0	1.0
0.5	1.07	1.71
1.0	1.11	2.0
1.5	1.20	2.22
2	1.30	2.41

Critical ignition temperature for high activation energies and various orders of reaction (fibre insulating board)

These values of  $\theta_c$  have been derived by the approximation of equation (7) and are too low, the results (4) for  $m = 0$  being  $\theta_c$  equal to 1.2 - 1.61 for the slab and the sphere respectively, when the temperature distribution is not approximated. The results in Table I show, however, that the effect of oxygen diffusion on these values is not large.

3.3. The critical values of the ignition parameter  $\delta$ .

From these results we conclude that for low values of "m" the critical value of  $\theta_c$  is of order unity and that it is permissible to replace  $\exp -E/RT$  by  $\exp -E/kT_c = e^{-\theta}$  to a first approximation. We then have equation (8) becoming

$$\frac{E}{RT_c^2} (1+k)\bar{\alpha}_k A e^{-E/RT_c} = \frac{\theta e^{-\theta} (1+k)\bar{\alpha}_k}{(1-c\theta)^m} = \delta'$$

The left-hand side of this equation is similar to the well known parameter  $\delta$  which must be less than a maximum value  $\delta_c$  for ignition not to take place. For zero "m",  $\delta_c$  has the correct critical values of 0.88, 2.0 and 3.32 for the slab, cylinder and sphere (4). We define these values for zero "m" by  $\delta_0$  so that the critical value of  $\delta$ ,  $\delta'_c$  is obtained from the maximum value of  $\delta'/\delta_0$  where

$$\delta'/\delta_0 = \frac{\theta e^{-\theta}}{(1-c\theta)^m} \dots\dots (15)$$

Differentiation of equation (15) with respect to  $\theta$  gives the characteristic equation identical with equation (14) - the negative sign being taken. It has been pointed out above that for any "m" there is a maximum value of C above which there is no critical state. This therefore defines a maximum  $\delta c/\delta_0$  for each value of m. From equations (14) and (15) we obtain the following numerical results for three values of C, 0.1 and 0.2 and  $(1 + \sqrt{m})^{-2}$

TABLE 2  
Values of  $\delta c/\delta_0$

m	C = 0.1	C = 0.2	C = $(1 + \sqrt{m})^{-2}$
0	1.0	1.0	1.0
1	1.12	1.30	1.47
2	1.27	-	2.12
3	1.48	-	2.78

The effect of "m" on  $\delta c/\delta_0$  is not large for a first order reaction and the most important effect of the inclusion of mass transfer is to restrict the range of physical and chemical properties where critical values of  $\theta$  and  $\theta$  can occur.

### 3.4. The ignition jump

In connexion with Fig. 1 it was pointed out that heating the material slowly enough for it to be regarded as in equilibrium at each instant leads to a temperature jump from X to Y'.

Clearly the magnitude of the temperature jump  $\Delta T_{xy}$  can be calculated from equations (11), (12) and (13), and for m equal to unity and  $y = 0.4$  the result is shown in Fig. 2. The asymptotic formula for  $C=0$  is

$$\Delta T_{xy} = \frac{1}{B} = \frac{\Delta Q w_0}{K}$$

For fibre insulating board, the values listed above give  $\frac{E \Delta T_{xy}}{R T_0}$  equal to 12.4

$$\Delta T = 290^\circ\text{C}$$

with Penman's diffusion relation and  $190^\circ\text{C}$  with Dye and Dallaville's. This result will be affected too by the value assumed for Q which is only approximate and which will, moreover, be influenced by changes in the chemical reactions occurring after ignition, but clearly the temperature jump may be some two or three hundred degrees. Also thermal capacity effects will reduce this estimate, by an amount which cannot be calculated from this steady state theory. It is interesting to note that the upper limit for this jump is less than that set by the exhaustion of the reacting solid material - not taken into account in this theory. This limits the temperature jump to a maximum of  $Q/c$  where Q is the heat of reaction per unit mass of solid reactant and c is the specific heat. Q is of order  $100 \text{ cal/gm}$  for fibre insulating board, so  $Q/c$  is of order  $300^\circ\text{C}$ .



(9)  
From the results of Mitchell one would expect cubes of wood fibreboard to ignite at temperatures between 180°C and 260°C if the linear size is between 1/5 in. and 2 in. Over this range, which covers most experimental conditions the temperature jump on ignition would be expected to raise the temperature to about 550°C or less. There is thus a possibility that combustion of the solid carbonaceous char to ash could just occur.

#### 4. Discussion and conclusion

The self-heating equation for simultaneous heat and mass diffusion is derived in a form similar to that discussed by Buben (1) and the insertion of numerical values into the relevant parameters suggest that in discussing the conditions necessary for ignition in air, oxygen diffusion is not important for fibre insulating board nor therefore for dusts and sawdust where the porosity is greater, even if the reaction depends on the presence of oxygen. For wood, we should not expect a sharply defined or critical value unless the wood were of certain species and moreover had a significant proportion of end grain exposed. The effect on the critical parameter of any dependence of the reaction on oxygen is not likely to be significant for fibre insulating board.

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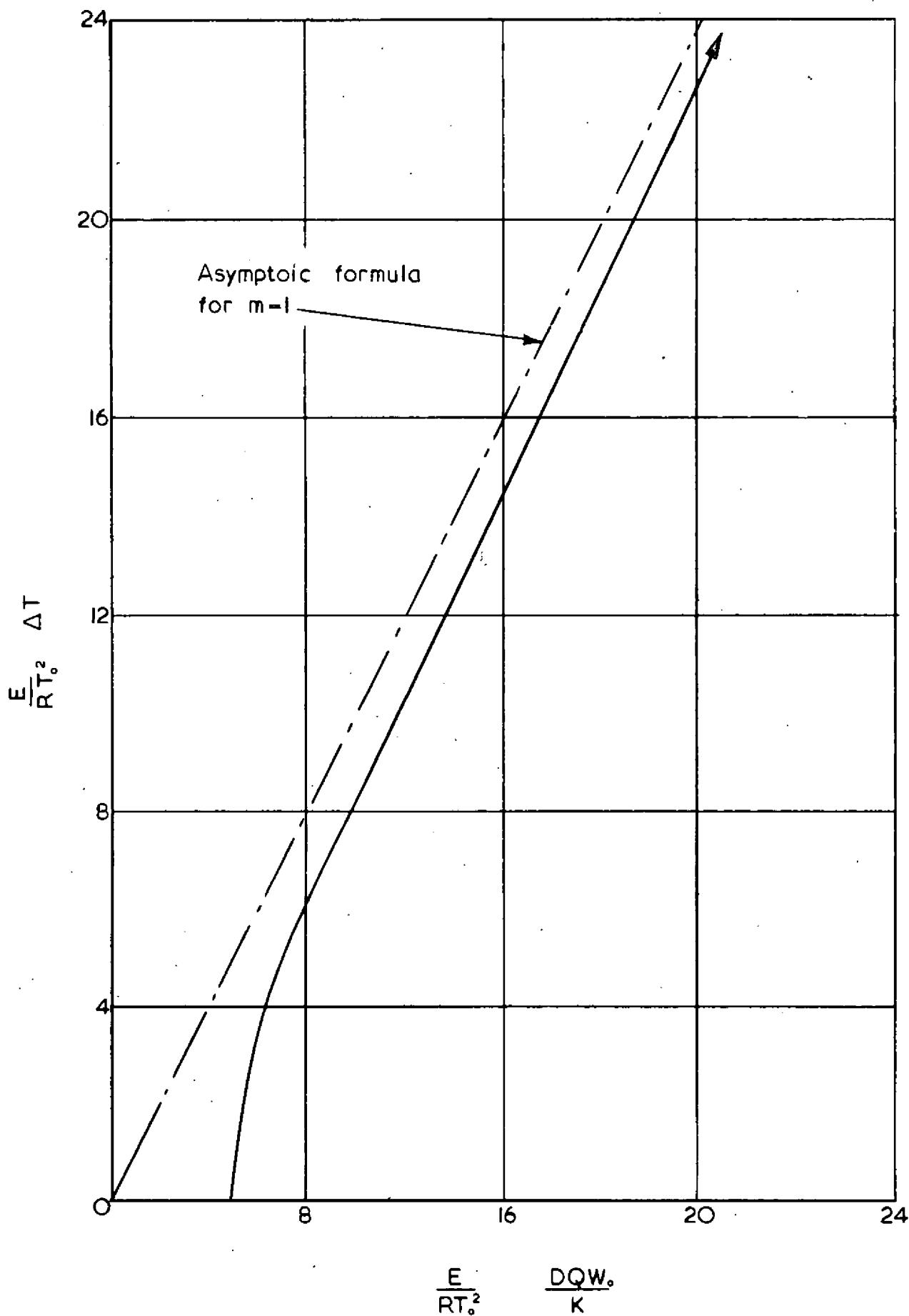


FIG. 2. THE TEMPERATURE JUMP AT IGNITION DUE TO OXYGEN LIMITATION