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A COMMENT ON THE THERMAL DECOMPOSITION OF WOOD
AT HIGH TEMPERATURES

by

P. H. Thomas

SUMMARY

In this paper some of the experimental data published by
Wright and Hayward[1] for the rates of thermal decomposition of
small cubes of wood of various sizes are discussed in terms of
theoretical considerations of heat transfer to the surface and
through the charcoal layer.

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INTRODUCTION

Wright and Hayward[1] measured the rates of decomposition of cubes of wood between 3 and 19 mm in size when they were suddenly immersed into vessels containing nitrogen maintained at temperatures of 500°C, 700°C and 900°C. Two kinds of wood (oven dried) were used, hemlock, density 0.43 and western red cedar, density 0.34 g/cc. The results were expressed as

$$100 \frac{d(P/P_\infty)}{dt} = k\sqrt{100\left(1 - P/P_\infty\right)} \tag{1}$$

where

$$k = \left(\frac{1}{\rho\ell} - 0.75\right)\left(0.00065\,T - 0.4\right) \tag{1A}$$

P = pressure in vessel at time 't'.

P_∞ = pressure at end of heating

k = "rate constant" sec^{-1} (sic)

T = absolute temperature of vessel

ρ = density of wood

ℓ = size of cube

t = time in seconds

In this paper these results are discussed in terms of the physical processes of heat and mass transfer.

In some subsidiary experiments Wright and Hayward showed that the rate of decomposition along the grain was twice that across the grain. One may presume this to be associated with the greater conductivity along the grain.

For a cube cut normally and along the grain decomposition across the grain occurs on four faces and along the grain on two. We denote the faster of the two mass rates of decomposition, i.e. the mean rate along the grain, by $\overline{m}''$ ($gcm^{-2}s^{-1}$) and assume that this is constant in time. We can then write the volume of the undecomposed wood at time t as

$$V_t = \ell^3\left(1 - \frac{\overline{m}''t}{w\rho\ell}\right)^2\left(1 - \frac{2\overline{m}''t}{w\rho\ell}\right) \tag{2}$$

where w is the fraction of the total mass of wood that volatalizes and is here taken as 0.6. Since the excess pressure in the vessel is proportional to the amount of volatiles.

$$P \propto V_0 - V_t \tag{3}$$

and

$$P_\infty \propto V_0$$

From these equations we obtain

$$\frac{d}{dt}\left(P/P_\infty\right) = \frac{4\overline{m}''}{w\rho\ell}\left(1 - \frac{\overline{m}''t}{w\rho\ell}\right)\left(1 - \frac{3\overline{m}''t}{2\rho w\ell}\right) \tag{4}$$

and

$$1 - P/P_\infty = \left(1 - \frac{\bar{m}''t}{\omega\rho\ell}\right)\left(1 - \frac{2\bar{m}''t}{\omega\rho\ell}\right) \quad (5)$$

From equations (4) and (5) we can write

$$\frac{d}{dt}\left(P/P_\infty\right) = \frac{4\bar{m}''}{\omega\rho\ell} f\left(1 - P/P_\infty\right) \quad (51)$$

Fig.1 shows $f(1 - P/P_\infty)$ as a function of $(1 - P/P_\infty)$. Also on the same graph are shown $(1 - P/P_\infty)^{1/2}$ and $(1 - P/P_\infty)^{2/3}$ and it is seen that the calculated relation is intermediate between them. A better agreement with Wright and Hayward's equation would be obtained by adopting some factor other than 2 for the ratio of the decomposition rates in the two directions. However, the average difference between $(1 - P/P_\infty)^{1/2}$ and the curve calculated on the assumption of a constant value of $\bar{m}''$ is only about 10 per cent, and accordingly we write as an approximation

$$\frac{d}{dt}\left(P/P_\infty\right) \doteqdot \frac{4\bar{m}''}{1.1\,\omega\rho\ell}\left(1 - P/P_\infty\right)^{1/2} \quad (6)$$

Comparing equations (1) and (6), we obtain the value of the faster of the two rates of decomposition as

$$\bar{m}'' \doteqdot \frac{1.1\,\omega}{40}\left(1 - 0.75\rho\ell\right)\left(0.00065\,T - 0.4\right) \quad (7)$$

Clearly the slight quantitative discrepancy between this formulation of the decomposition of the cubes and that of Wright and Hayward is not, in practice, a significant one. For example, no attention has been paid to the "rounding" of the corners or edges of the cubes. Nevertheless, it is preferable to regard the decomposition as the result of a linear or almost linear charring rate than in terms of a theory which is formulated in kinetic terms. It appears inappropriate to discuss a kinetic law for the whole volume when decomposition takes place in a zone. The reactions in this zone could of course be discussed kinetically.

The significance of the cube size is here a small correction to a charring rate, not a major term in a "rate constant".

A presentation in more explicitly chemical terms has been given by Tyul'panov[2].

Tyul'panov has performed experiments in which cubes were progressively heated in a furnace and he quotes the following formula for the rate of decomposition.

$$\frac{dv}{dt} = \frac{2}{3}\, e^{-E/RT}(1 - v)^2 \quad (8)$$

where E is an activation energy
R is the universal gas constant
v is a concentration

The unit of time has been changed here from minutes to seconds. The value given for E over the temperature range $300^\circ - 900^\circ C$ is a low one — 6,300 cal/gm. mole and it is interesting to note that this is close to the value (5,800) given when Wright and Hayward's data are plotted on an Arrhenius plot, (see Fig.2) and the Stefan-Boltzman radiation law gives an

apparent value of this order. It seems that Tyul'panov's activation energy expresses a dependence on temperature which is explained on physical not chemical grounds. The very low value of the rate constant $\frac{2}{3}$ supports this. The second order form of equation (8) may be a reflection of the decrease in rate due to the increasing depth of char.

The experimental results show that this mean rate, $\bar{m}''$, decreases as $\rho\ell$ increases. The values $\rho\ell$ varied between 0.1 and 0.8 so that $\bar{m}''$ varies by a factor of about 2.3 over the whole range of thicknesses. Some of this variation is probably due to the larger cubes forming larger depths of char, which results in a lowering of the heat flux to the reaction zone. The formation of an insulating char layer will reduce the heat transfer to the reaction zone and the rate of propagation of this zone will decrease with time. (See below). So that as little error as possible arises from this effect we shall discuss at first only the results for the smallest cubes. Also the convective heat transfer is dependent on the size of the cube but this cannot account for the effect of size at the higher temperatures where radiation is predominant. We shall now consider some of the implications of these values of $\bar{m}''$.

Mass Transfer Theory

For mass transfer we use the formula[3] which is derived from the treatment given by Spalding for a drop of liquid fuel.

$$\frac{\bar{m}''\ell C_s}{K_g} = 0.65 \left(\frac{g\,\ell^3}{\nu^2}\right)^{1/4} \log_e (1+B) \tag{9}$$

ℓ is the diameter of the spherical drop which we shall regard as equal to the side of a cube.

B   is the transfer number

g   the gravitational acceleration

K_g the thermal conductivity of the gases

ν the kinematic viscosity

and Cs   the specific heat of the liquid or solid.

Where there is no combustion, B, as in these experiments done in nitrogen, is given by

$$B = \frac{C_g (T_g - T_s)}{Q_o} \tag{10}$$

where C_g is the specific heat of the gas

T_g the environmental temperature

T_s the surface temperature

and Q_o is the diffusional and convected heat required to transfer 1 gm of substance from the surface.

We shall regard wood as decomposing at a fixed temperature* - T_c - and neglect the small difference between cubes and spheres. Rapid decomposition

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*Strictly speaking wood decomposes over a range of temperature depending on the heating conditions. An analysis taking this into account would be greatly complicated and in view of other uncertainties in the property values and their variation with temperature which is not taken into account in deriving equation (9) it is sufficient to assume a fixed charring temperature for the purposes of this paper.

produces little or no heat of decomposition[4], indeed, the reaction may be endothermic so that we write

$$Q_0 = Q_s - \frac{I}{\overline{m}''} - q \qquad (11)$$

where q is the exothermic heat release per gm of transferred substance which may be negative[4]

I is the net radiation received

and Q_s is the heat content of the gases leaving the solids of the residue, per gm of volatiles.

Table 1 gives the numerical values adopted. The gases evolved are assumed to be similar to ethylene in physical properties, the values of temperature dependent quantities being taken at the mean temperature $\frac{T_0 + T_g}{2}$.

TABLE 1

Property Values Assumed

	500°C	700°C	900°C
c_s	0.34	0.34	0.34
c_g	0.77	0.81	0.89
w	0.6	0.6	0.6
K_g	2.0×10^{-4}	2.4×10^{-4}	2.9×10^{-4}
ρ_g	5.5×10^{-4}	4.8×10^{-4}	4.3×10^{-4}
ν	0.47	0.62	0.76

We have also $I = \delta (T_g^4 - T_s^4)$ (12)

where δ is the Stefan-Boltzman constant

To perform calculations we must define Q_s. If the volatiles emerge at T_c unheated by passing through the char layer

$$Q_s = Q_{s,1} = \frac{c_s (T_c - T_0)}{\omega} + \left(\frac{1}{\omega} - 1\right) c_s (T_s - T_c) \qquad (13)$$

where T_0 is the initial temperature of the wood, but if emerging at T_s - perfect heat exchange between volatiles and char

$$Q_s = Q_{s,2} = \frac{c_s (T_s - T_0)}{\omega} + (c_g - c_s)(T_s - T_c) \qquad (14)$$

Firstly, taking a mean ν of 0.4 we calculate from equation (7) the value of $\overline{m}''$ when ℓ is 3 mm - the 'observed' value of $\overline{m}''$. We then insert this into equation (9) to obtain Q_0. With I given by equation (12) - assuming $T_s^4 \ll T_g^4$ we calculate maximum possible values for $Q_s - q$, the net external heating required to produce 1 gm of volatiles. These are given in Table 2.

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TABLE 2

Calculated Values of Qs_1, Qs_2 and $Q_S - q$
(based on data for $\mathcal{l} = 3$ mm)

$\bar{m}''$ from equation (7) $g\ cm^{-2}s^{-1}$	T_g	$Q_S - q$ cal/gm	$Qs_1\ (T_g)$	$Qs_2\ (T_g)$
0.0015	500°C	340	204	358
0.0035	700°C	350	250	562
0.0055	900°C	470	296	830

If $T_S^4 \ll T_g^4$ the calculations suggest that q becomes smaller as the temperature rises, i.e. as the rate of decomposition increases. This is qualitatively in accordance with the findings of Klason[4].

Also in Table 2 are given values of Qs_1 and Qs_2 calculated as maximum values assuming $T_S = T_g$.

The value of $\mathcal{l}$ and hence of $Q_S - q$ is not very sensitive to the value of T_S until values approaching within about 200°C of T_g are involved.

The minimum values of Qs_1 and Qs_2 are obtained by putting $T_S = T_o$. They are then the same and equal to 160 cal/gm. between $\frac{1}{2}$ and $\frac{1}{4}$ of the value calculated for $Q_S - q$.

The values of $Q_S - q$ calculated from Wright and Hayward's data for the heating across the grain would be about twice the values quoted in Table 2 and would be larger for larger cubes.

Clearly a precise value of T_S and the extent of the heat exchange between the char and the stream of volatiles are necessary before any estimate, even if its sign, can be made of q.

It is not a straightforward matter to decide whether this heat exchange is significant or not because the pores in the char layer appear to consist characteristically of large and small pores and the volatiles may preferentially emerge from the cracks with less heat exchange than if one assumed all pores to be the same size. Some experiments are in progress to study this question.

However, the two extreme situations may be separately considered in an attempt to evaluate T_S.

THE EFFECT OF THICKNESS OF CHAR

The results of Wright and Hayward show that $\bar{m}''$ varies with cube size as in equation (7) and here we set out to develop an expression for the effect of charcoal thickness on $\bar{m}''$. Consider the assumption that the volatiles are not heated by the charcoal residue.

The heat transferred to unit area of the reaction zone across a layer of thickness Δ is $\frac{Kc}{\Delta}$ ($T_S - T_c$) per second, where Kc is the thermal conductivity of the charcoal and this raises the temperature of $\frac{m''}{w}$ gm per second of wood by ($T_c - T_o$). m'' is the instantaneous rate of decomposition.

Therefore, allowing for exothermic heating

$$\Delta = \frac{K_c\, \omega}{c_s\, m''} \cdot \frac{(T_s - T_c)}{(T_c - T_o - q/c_s)} \tag{15}$$

If heat exchange were perfect between the stream of volatiles and the char, we would have instead of equation (15)

$$\Delta = \frac{K_c}{c_s\, m''}\, \log_e \left(1 + \frac{c_g\,(T_s - T_c)}{c_s\,(T_c - T_o - q/c_s)} \right) \tag{16}$$

by an analysis practically the same as that of Spalding's "stagnant film hypothesis" where Δ is the "boundary layer" and $\dfrac{c_g\,\omega\,(T_s - T_c)}{c_s\,(T_c - T_o - q/c_s)}$ the effective B. Equations (11) and (12) give

$$Q_s - q = \frac{\sigma(T_g^4 - T_s^4)}{m''} + Q_o \tag{17}$$

where Q_s is given by either equation (13) or (14) according to whether we assume the volatiles are heated or not by the char residue. By definition we have

$$m'' = \rho\omega\,\frac{d\Delta}{dt} \tag{18}$$

Consider the case of no heat exchange between volatiles and char. Equation (13) is rearranged as

$$\begin{aligned}
Q_s = Q_{s.1.} &= \frac{c_s(T_g - T_o)}{\omega} - c_s(T_g - T_c) \\
&\quad - c_s(T_g - T_s)\left(\tfrac{1}{\omega} - 1\right) \\
&= Q_{s.1}(T_g) - c_s(T_g - T_s)\left(\tfrac{1}{\omega} - 1\right)
\end{aligned} \tag{19}$$

where $Q_{s1}(T_g)$ is given in Table 2.

We have from equations (17) and (19), neglecting Q_o, which from equations (9) and (10) is virtually zero when $T_g = 700^\circ C$ or $900^\circ C$ and only about 10 cal/gm for $T_g = 500^\circ C$.

$$\begin{aligned}
m'' &= \frac{\sigma(T_g^4 - T_s^4)}{Q_{s1}(T_g) - q - c_s(T_g - T_s)\left(\tfrac{1}{\omega} - 1\right)} \\
&\approx \frac{\sigma(T_g^4 - T_s^4)}{Q_{s1}(T_g) - q}\left(1 - \frac{c_s(T_g - T_s)\left(\tfrac{1}{\omega} - 1\right)}{Q_{s1}(T_g) - q} \right)^{-1}
\end{aligned} \tag{20}$$

The approximation

$$\sigma(T_g^4 - T_s^4) \doteq 4\sigma(T_g - T_s)\,T_g^3$$

is satisfactory for $T_g \sim T_s$ but if $T_s \ll T_g$ the right hand side is 4 times too large. We shall therefore introduce a "constant" p, $\tfrac{1}{4} < p < 1$ to accommodate departures from the approximation.

Thus equation (2) becomes

$$m'' \doteq \frac{4p\,\sigma\,T_g^3\,(T_g - T_s)}{Q_{s1}(T_g) - q}\left(1 - \frac{c_s(T_g - T_s)\left(\tfrac{1}{\omega} - 1\right)}{Q_{s1}(T_g) - q} \right)^{-1} \tag{21}$$

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The mean value in time of m'' corresponds (at least in so far as the first major term on the right-hand side is concerned) to the mean value of T_s and from equations (15) and (18) the mean value of $\Delta m''$ corresponds to the product of $\bar{m}''$ and $\dfrac{\Delta max.}{2}$ i.e. $\ell/4$, that is, from equation (15)

$$\frac{\ell c_s \bar{m}''}{4} \left(\frac{T_c - T_o - q/c_s}{K_c \omega} \right) = (T_q - T_c) - (T_q - \bar{T_s})$$

$$= (T_q - T_c) - \frac{\bar{m}'' (\phi_{s_i}(T_q) - q)}{4 p \sigma T_q^3} \left(1 + \frac{\bar{m}'' c_s (1/\omega - 1)}{4 p \sigma T_q^3} \right)^{-1} \tag{22}$$

We shall make use of the following inequality in simplifying some second order magnitude terms

$$c_s (T_q - T_c)(1/\omega - 1) \lll \phi_{s_i}(T_q) - q$$

The maximum possible value of the left-hand side of this inequality is $0.34 \times 0.67 \times 600 \approx 136$ which is about $\frac{1}{4}$ of the right-hand side. For $T = 500°C$ the maximum value of the left-hand side is 46, about $\frac{1}{8}$ of the corresponding right-hand side value. The approximation is therefore usable. With this approximation it may be shown that equation (22) reduces to

$$\bar{m}'' = \frac{(T_q - T_c)}{a + b - d(T_q - T_c)} \left\{ 1 - \frac{ad(T_q - T_c)}{[a + b - d(T_q - T_c)]^2} \right\} \tag{23}$$

where $\quad a = \dfrac{c_s (T_c - T_o - q/c_s)\ell}{4 K_c \omega} \tag{24}$

$$b = \frac{\phi_{s_i}(T_q) - q}{4 p \sigma T_q^3} \tag{25}$$

and $\quad d = \dfrac{c_s (1/\omega - 1)}{4 p \sigma T_q^3} \tag{26}$

Hence equation (23) can be written as

$$\bar{m}'' = \bar{m}_o'' \left\{ 1 - \frac{c_s (T_c - T_o - q/c_s) p \sigma T_q^3 \ell}{K_c \omega (\phi_{s_i}(T_q) - q)} \left(1 + \frac{c_s (T_q - T_c)(1/\omega - 1)}{\phi_{s_i}(T_q) - q} \right) \right\} \tag{27}$$

$$\bar{m}_o'' = \frac{4 p \sigma T_q^3 (T_q - T_c)}{(\phi_{s_i}(T_q) - q)} \left\{ 1 + \frac{c_s (1/\omega - 1)(T_q - T_c)}{\phi_{s_i}(T_q) - q} \right\} \tag{28}$$

Equation (27) which is an approximation for small ℓ is of the same form as that found by Wright and Hayward shows that the coefficient of ℓ in the expression for the variation of $\bar{m}''$ with ℓ is greater than

$$\alpha = \frac{(T_c - T_o - q/c_s) p \sigma T_q^3 c_s}{K_c \omega [\phi_{s_i}(T_q) - q]}$$

Neglecting the value of $\dfrac{C_s(T_g - T_c)(\frac{T_c}{T_0} - 1)}{\Phi_r(T_g) - q}$ c.f. unity which as we have seen above is at most a 25 per cent error in the coefficient α, we have from equation (28)

$$\alpha \doteq \frac{\bar{m}_o''}{4} \frac{(T_c - T_s - q/c_s)}{(T_g - T_c) K_c w} \qquad (29)$$

The values of $\bar{m}''$ given in Table 2 are approximately proportional to $T_g - T_c$ so that α is approximately independent of T_g for a constant K_c and q. If we take the values of $\bar{m}''$ given in Table 2 for the 3 mm cube the mean value of α from equation (29) is, with $K_c \doteq 2 \times 10^{-4}$ c g s units

$$\alpha \doteq \frac{0.0035}{4 \times 10^{-4} \times 2 \times 0.6} \left(1 - \frac{q}{C_s(T_c - T_s)}\right) \times \frac{300}{400}$$

$$\sim 5.3 \left(1 - \frac{q}{C_s(T_c - T_s)}\right)$$

Thus, if q is zero, α is at least one order greater than the experimentally found value which was $0.75\rho \sim 0.3$ and despite our approximations we must conclude that either $q \approx C_s(T_c - T_0)$ i.e. the material is exothermic to about 100 cal/gm or the thermal conductivity of charcoal is much larger than the value assumed here. The former assumption leads to maximum values of Q_s of 440, 450 and 570 cal/gm for the three temperatures 500°C, 700°C and 900°C, values still consistent with those estimated in Table 2 for $Q_s.1$ and $Q_s.2$ but implying that there is considerable heat exchange between the volatiles and the char. Alternatively that there is considerable radiation transfer through the charcoal residue.

Had we used equation (16) instead of equation (15) these conclusions would still apply qualitatively because equation (16) can be regarded as equivalent to equation (15) with a variable, but nevertheless reduced, value of K_c and thus it would lead to a greater coefficient for the effect of ℓ on $\bar{m}''$, not less as is required for compatibility with the experimental data.

Conclusions

1. Wright and Hayward's data may be interpreted as the result of rate of charring almost constant in time. The variation of decomposition rate with temperature and Tyul'panov's data are consistant with a physical rather than a chemical rate constant. We have not attempted here to discuss the difference in behaviour across and along the grain. This could well invoke a more detailed discussion of the true kinetics of the reaction zone and the transient heat balance of the reaction zone proper.

2. Values deduced from this data for the heat to release 1 gm of volatiles are of the order calculated by assuming wood char at 300°C, without allowing for exothermic or endothermic heating; although this may be a factor in the process of decomposition there are too many uncertainties to decide this question definitely with these data.

3. The experimental variation of $\bar{m}''$ with cube size suggests either an exothermic reaction of order 100 cal/gm or an effective thermal conductivity of the charcoal layer, about an order greater than that assumed, i.e. the effect is consistent with a K of order 4×10^{-3} rather than 2×10^{-4} c.g.s. units as assumed here or some combination of these two factors.

Acknowledgement

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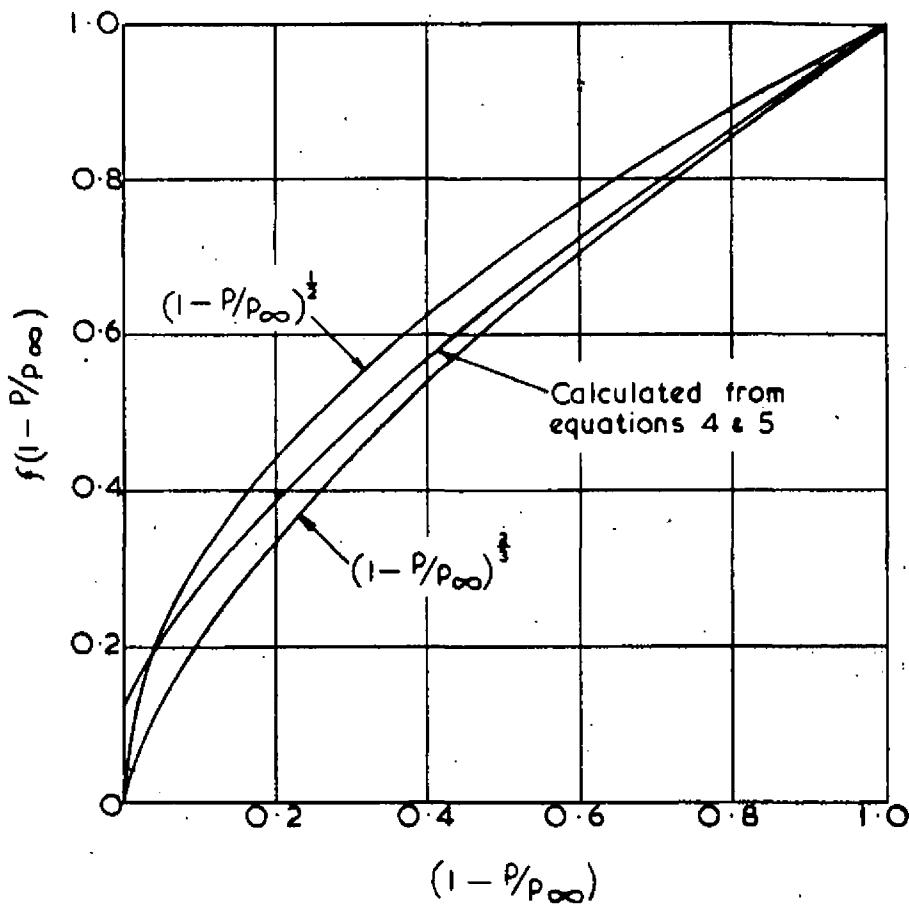4. KLASON, P. Gidolizi Lesokhim Prom., 1957, 10 (6) 13.

FIG.I. COMPARISON OF $\frac{1}{2}$ AND $\frac{2}{3}$ KINETIC LAWS
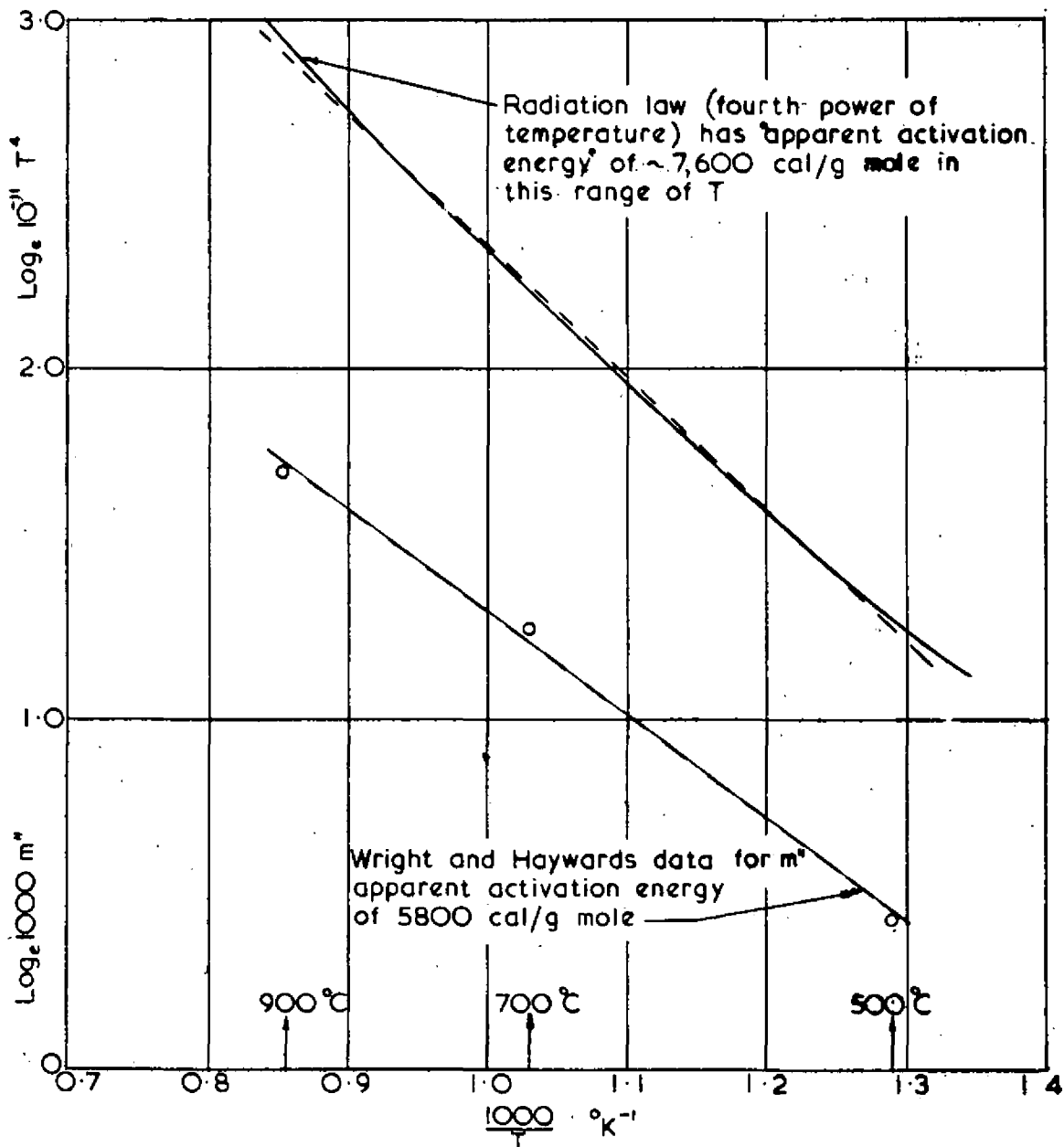WITH CONSTANT CHARRING RATE

FIG.2. WRIGHT AND HAYWARD'S DATA AND FOURTH POWER
RADIATION LAW SHOWING AN APPARENT OBEDIENCE