DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH AND FIRE OFFICES' COMMITTEE
JOINT FIRE RESEARCH ORGANISATION

ESTIMATES OF THE RATE OF HEAT EVOLUTION AND OF THE ACTIVATION ENERGY FOR
A STAGE IN THE IGNITION OF SOME WOODS AND FIBREBOARD

by

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Summary

Temperature/time records for spontaneous heating in the
temperature range 200 - 300°C during ignition of some woods and
wood fibreboard have been used to obtain estimates of the rate of
heat evolution and the activation energy.

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September, 1956.

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1. INTRODUCTION

A previous note [1] describes the determination of the ignition temperatures of a number of different woods and wood fibreboard. The experimental conditions under which the determinations were made, and the main observations on the behaviour of the materials during ignition, are relevant to the present note and are summarised below.

A specimen of the raspings of a wood was packed into a tube supported in an electric furnace. Air, preheated to near the furnace temperature, was passed through the specimen at a constant rate while the furnace was heated from room temperature at constant power.

The behaviour of the temperature at the centre of the specimen (as measured by a thermocouple), in a typical determination is shown in Fig. 1; the specimen in this case was oak. An exothermic reaction began to affect the course of the specimen temperature record above a temperature of about 150°C. The rise in specimen temperature then accelerated, overtook that of the furnace and eventually became very rapid as the temperature rose to high values associated with glowing combustion of the specimen.

The first visible evolution of volatile decomposition products from the specimen occurred in the early stages of the exothermic reaction. The rate of evolution increased with rising temperature until, coinciding with the period of most rapid temperature rise in the specimen, there was a relatively sudden and copious evolution of thick tarry smoke that lasted for little more than a minute. Flame did not appear under the conditions of these tests; presumably the volatiles were evolved at a temperature too low for their spontaneous ignition, since it was possible to ignite the volatiles by means of a pilot flame during their evolution at the higher rates.

In the present note the temperature/time records (as Fig. 1.), for some different species of wood and for wood fibreboard are used, with corrections for heat transfer between the specimen and the furnace, to calculate the net rate of evolution of heat at a series of temperatures during the spontaneous heating in the temperature range of about 200 - 300°C. Estimates are then made of the activation energy for the process, i.e. the constant E in the Arrhenius equation for the temperature dependence of the reaction rate constant

$$k = \emptyset \ e^{-E/RT} \qquad \ldots \ldots \ldots (1)$$

in which

      k = reaction rate constant,
      $\emptyset$ = constant,
      R = gas constant,
      T = absolute temperature.

2. CALCULATION OF THE NET RATE OF EVOLUTION OF HEAT

2.1. Basis of calculation

For the present purpose the instantaneous net rate of heat evolution, q, in a region of thermal capacity C, surrounding the thermocouple in the specimen may be expressed as follows [1]:-

$$\frac{q}{C} = \frac{q_e - q_l}{C} = \frac{d\theta_s}{dt} - \frac{hA}{C}(\theta_f - \theta_s) \qquad \dots \dots (2)$$

where

q_e = actual rate of heat evolution in the region considered at time t,

q_l = rate of heat loss from region at time t (largely in volatile products of reaction),

θ_s = temperature of specimen in region at time t,

θ_f = furnace temperature at time t,

h = a heat transfer coefficient,

A = boundary area of region considered.

The second term on the right hand side of equation (2) represents the rate of heat transfer between the furnace and the region of the specimen under consideration. This heat transfer involves conduction, natural and forced convection, and radiation, and the factor hA/C must be expected to vary over any but small ranges of temperature.

The quantity q/C may be calculated if experimental values for the other terms in equation (2) are available.

2.2. The factor hA/C

For an inert material heated in the ignition furnace the quantity q/C will be zero, and instantaneous values of the factor hA/C may be calculated from values of θ_f, θ_s and $d\theta_s/dt$ that correspond in time*. This has been done, in the first place, for a specimen of dry sand. The results are shown in Fig. 2 where it will be seen that the factor hA/C increases linearly and relatively slowly as the specimen temperature increases over a wide range (40 - 300°C).

It has been shown that the rate of evolution of heat when wood sawdust is heated in an atmosphere of nitrogen up to a temperature of about 300°C is negligible compared with the evolution of heat that occurs when the sawdust is heated in air [1]. Thus the condition $q/C = 0$ is approximately realised for sawdust in an atmosphere of nitrogen and the factor hA/C may be determined as for dry sand above. Values determined for oak sawdust in a current of nitrogen, but otherwise under the same conditions as in a determination of ignition temperature, are shown in Fig. 3. The relationship of hA/C to the temperature of the specimen appears to be somewhat more complex than for sand but it can be taken as linear over the temperature range that is of interest here, about 200 - 300°C. Similar relationships were obtained for the other woods and for fibreboard heated in nitrogen. In most cases hA/C increased from about 0.09 to 0.13 as the specimen temperature increased from 200 to 300°C.

Using values of hA/C obtained as above the quantity q/C was calculated at a series of temperatures for the woods and fibreboard heated in air. The results are given in section 4.

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* θ_s and θ_f used in the calculations were mean values for the time intervals for which the corresponding values of $d\theta_s/dt$ were calculated.

2.3. Systematic errors in calculation of q/C

Because of a change in the heat transfer by conduction within the specimen and, also, because of a probable change in the thermal capacity, values of hA/C determined for heating in nitrogen will, when used to calculate q/C for heating in air, be increasingly in error as the rate of exothermic reaction in the specimen increases. However, since the correction term $(\theta_f - \theta_s)$ hA/C passes through zero in the temperature range that is of interest, and $d\theta_s/dt$ becomes relatively large, it is clear that q/C must become insensitive to errors in hA/C. That this is so is shown in Fig. 4, which gives the error in hA/C that would be required to produce an error of 1% in q/C for the temperature range 200 - 300°C in the heating of oak and fibreboard, assuming for the purpose that other errors are negligible.

The curve for oak in Fig. 4 may be regarded as typical for the woods tested. Up to about 220°C errors in hA/C will result in errors of similar relative magnitude in q/C, but at higher temperatures errors must rapidly become very large if they are to have any effect. At the lower temperatures the rate of heat evolution is small and errors due to the causes given above will be small also. It is concluded that, for the woods, q/C will be free from appreciable systematic error over the whole temperature range 200 - 300°C. For the fibreboard, however, q/C is sensitive to errors in hA/C for over half the temperature range and it is possible that a systematic error will make itself felt.

3. DETERMINATION OF THE ACTIVATION ENERGY

3.1. Basis of the calculation

The rate of heat evolution, Q, at time t and temperature $T°K$ in an exothermic reaction is given by equation (3), which combines a general equation for rate of reaction with the Arrhenius equation for the rate constant (1).

$$Q = H \frac{dc}{dt} = H \phi c_1^{n_1} c_2^{n2} \ldots e^{-E/RT} \qquad \ldots \ldots (3)$$

In (3)

H = heat of reaction,
c = molar concentration of the reactant or product in terms of which the progress of the reaction is followed;
c_1, c_2 = molar concentration of reactants 1, 2 ...,
n_1, n_2 = order of reaction with respect to reactants 1, 2 ...

In the ignition of sawdust in a plentiful supply of air (as under the experimental conditions of the present work) it is probable that the concentrations of reactants that affect the rate may be regarded as constant over an appreciable period of time. If this is so, and the heat of reaction is constant in the temperature range T_1 to T_2 °K, the activation energy may be calculated from the rates of heat evolution Q_1 and Q_2 at temperatures T_1 and T_2 respectively as follows:

$$E = 2 \cdot 303R \frac{\log_{10}Q_2 - \log_{10}Q_1}{1/T_1 - 1/T_2} \text{ cal/mol} \qquad \ldots \ldots (4)$$

Q_1 and Q_2 are, in practice, values taken from a plot of experimental values of $\log_{10}Q$ vs. $1/T$.

The measure of the rate of heat evolution in the sawdust that is available here is the net quantity q/C, or $(q_c - q_1)/C$.

The heat loss, q_l, includes the heat lost in volatile reaction products and heat lost to the thermocouple. The magnitude of this heat loss is not known, but if it can be assumed to be at all times small compared with the true rate of heat evolution, q_e, we have

$$q/C \approx q_e/C$$

Multiplying the above by the specific heat of the sawdust we have $q/m \approx q_e/m$ as a measure of the rate of heat evolution per unit mass; where m is the mass of the sawdust in the region surrounding the thermocouple.

A plot of $\log_{10} q/m$ vs. $1/T$ has been used to determine the activation energy by means of equation (4).

Since the specific heat of the sawdust, and its variation, in the temperature range 200 – 300°C was not known it was assumed to be constant with a value of 0·34. If, as here, the specific heat is taken as constant it is, of course, immaterial whether q/C or q/m is used for the determination of activation energy. But it is of interest to have values of the rate of heat evolution that are, at least, of the right order of magnitude; q/m has therefore been used.

3.2. Systematic error in calculation of activation energy

Sources of systematic error that will affect the calculated activation energy are variation in the pre-exponential factors in equation (3) (contrary to the present assumption that they are constant), and systematic error in the quantity q_e/m. The latter quantity will be subject to systematic error if, as is probable, the specific heat of the system varies and if the heat loss, q_l, is not negligible throughout the temperature range covered. Also, since loss in weight of the system during the ignition process will tend to represent loss in reactive solid rather than total solid, q_e/m will not be altogether independent of any loss in weight that occurs. It has already been seen that results for fibreboard may be affected by possible systematic error in the factor hA/C.

It is not possible to estimate the magnitude of the above sources of error and to correct for them. A systematic error thereby introduced into the calculated rate of heat evolution will affect the calculated activation energy in so far as the error is not a constant fraction of the heat evolution. The effect of such an error on the calculated activation energy can be relatively small, as can be seen from a determination of the effect of a single error in either Q_1 or Q_2 in equation (4); thus,

$$\Delta E \approx \frac{2 \cdot 303 \ R}{1/T_1 - 1/T_2} \cdot \frac{\Delta Q_2}{Q_2}$$

If we suppose ΔQ_2 is 20% of Q_2, $T_1 = 473$ and $T_2 = 573°K$, we have $\Delta E = 2300$ cal/mol. This amounts to a relative error of only about 8% on an activation energy of 30,000 cal/mol.

4. RESULTS

The plots of $\log_{10} q/m$ vs. $1/T$ for the series of woods and fibreboard are shown in Figs. 5–11. Except for the African mahogany, two experiments were carried out on each material; as an indication of the reproducibility, the results of the two experiments are distinguished by different symbols in some of the figures.

In all cases the experimental points lie about straight lines in
the temperature range of about 200 - 300°C. At the ends of this
temperature range the points for American whitewood and, perhaps, also
African mahogany and oak, tend to follow a curve concave to the axes.
It is not possible to decide whether this curvature is due to changes
in the reaction or merely to systematic errors of the kind described
above becoming appreciable at the ends of the temperature range.

Activation energies obtained from these plots, together with the
rates of heat evolution per gram of sawdust at 250°C, are given in
Table 1.

Table 1

Activation energies and rates of heat evolution

Specimen	Activation energy $cal\ mol^{-1}$	Heat evolution at 250°C $cal\ min^{-1}g^{-1}$
Oak (Quercus robur)	23,200	4.1
Iroko (Chlorophora excelsa)	33,000	3.9
Western red cedar (Thuja plicata)	31,000	3.2
African mahogany (Khaya ivorensis)	31,500	2.7
Beech (Fagus sylvatica)	28,800	2.6

American whitewood
    (Liriodendron tulip-
                    ifera)
	25,200	2.5

Fibreboard	16,000 (a) 29,800 (b)	1.06

(a) 200 - 300°C, (b) 280 - 350°C.

Fibreboard differs from the woods in that the activation energy
in the temperature range 200 - 300°C, and the rate of heat evolution at
250°C are markedly lower. Also there appears to be an increase of
activation energy at a temperature between 280 and 300°C; in the temper-
ature range 200-350°C the activation energy is similar to that for wood
in the range 200-300°C.

When the rate of heat evolution is small, heat losses are likely
to be relatively more important and their neglect will lead to estimates
of q_e being too low at the higher temperatures and, hence, to a value of
the activation energy that is too low. Also, errors in the factor hA/C
will probably be in the direction of overestimation and will lead to low
values of the activation energy at temperatures below the crossing point
which, for fibreboard, is 287°C. Whilst the differences between the fibre-
board and the woods may thus, to some extent, be due to systematic errors it is
thought that the differences are too large to be due entirely to such
errors: in order to double the activation energy the numerical values
of the rate of heat evolution would have to be squared.

Of the activation energies for the woods, those for oak and American whitewood, 23,000 and 25,200 cal/mol respectively, appear to be significantly lower than for the rest, which lie within 8% of 31,000 cal/mol.

No conclusions about the nature of the ignition reactions are drawn; values of the rate of heat evolution and activation energy are of use in theoretical treatments of ignition.

ACKNOWLEDGMENTS

The author is indebted to Mr. G. Skeet, Mr. A. J. Kelly, Miss M. Ward and Miss S. Townshend who have assisted from time to time in this work.

REFERENCES

1. BOWES, P. C. The determinations of the ignition temperature of solids by a rising temperature method. Department of Scientific and Industrial Research and Fire Offices' Committee Joint Fire Research Organization. F. R. Note No. 10/1952.

ERH
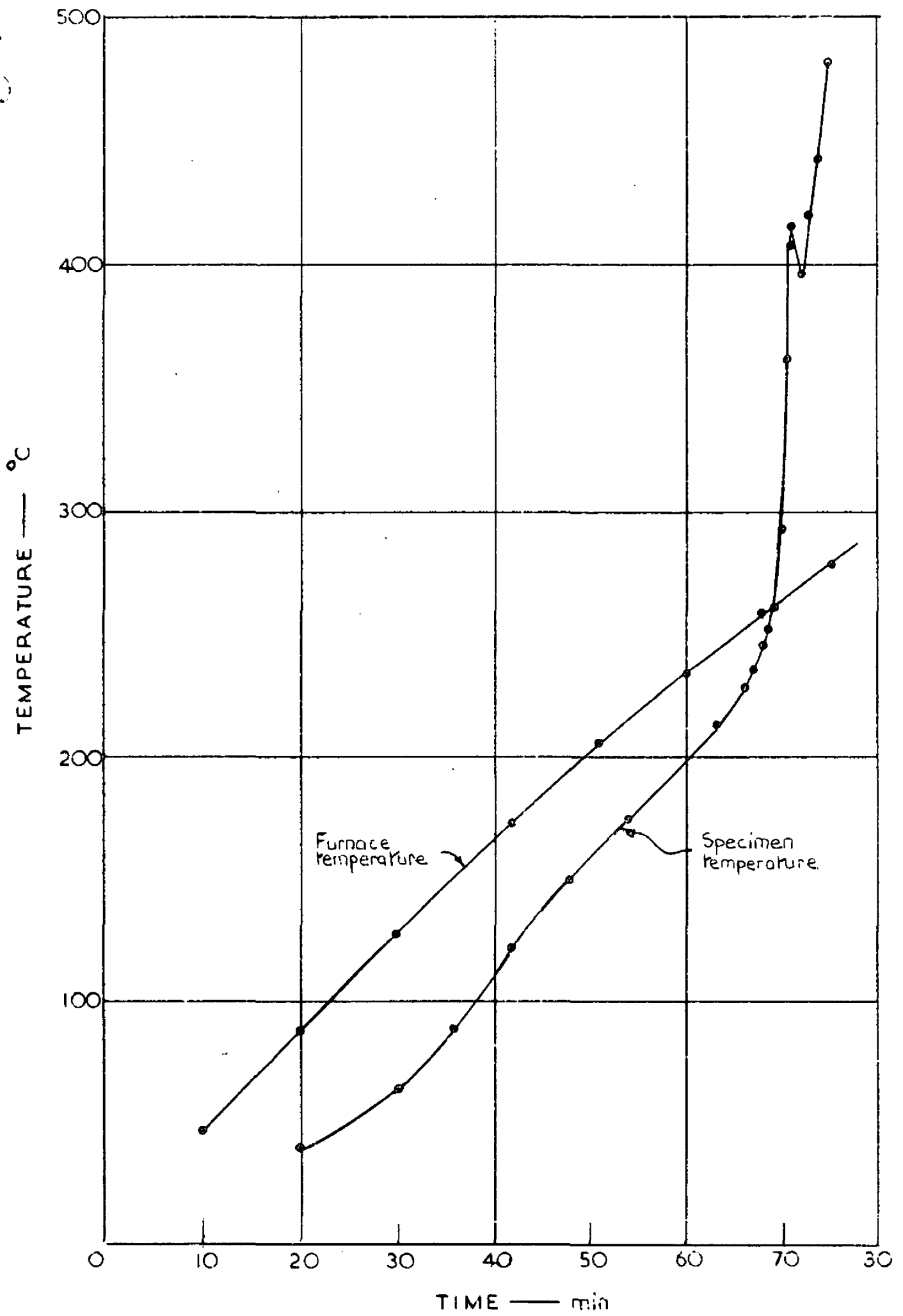
FIG.1. HEATING OF OAK SAWDUST
IN IGNITION FURNACE

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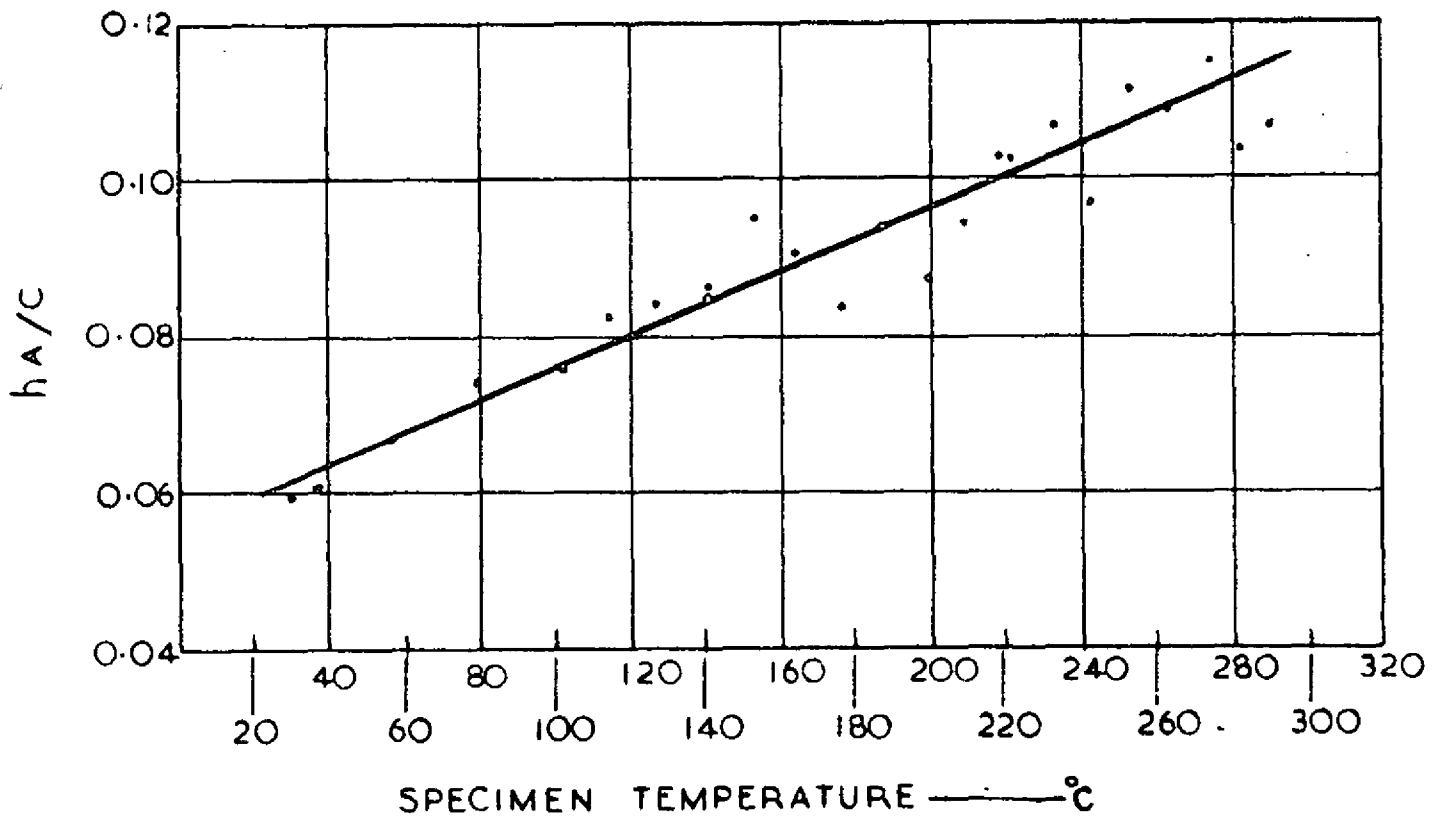
FIG.2. FACTOR hA/C FOR DRY SAND
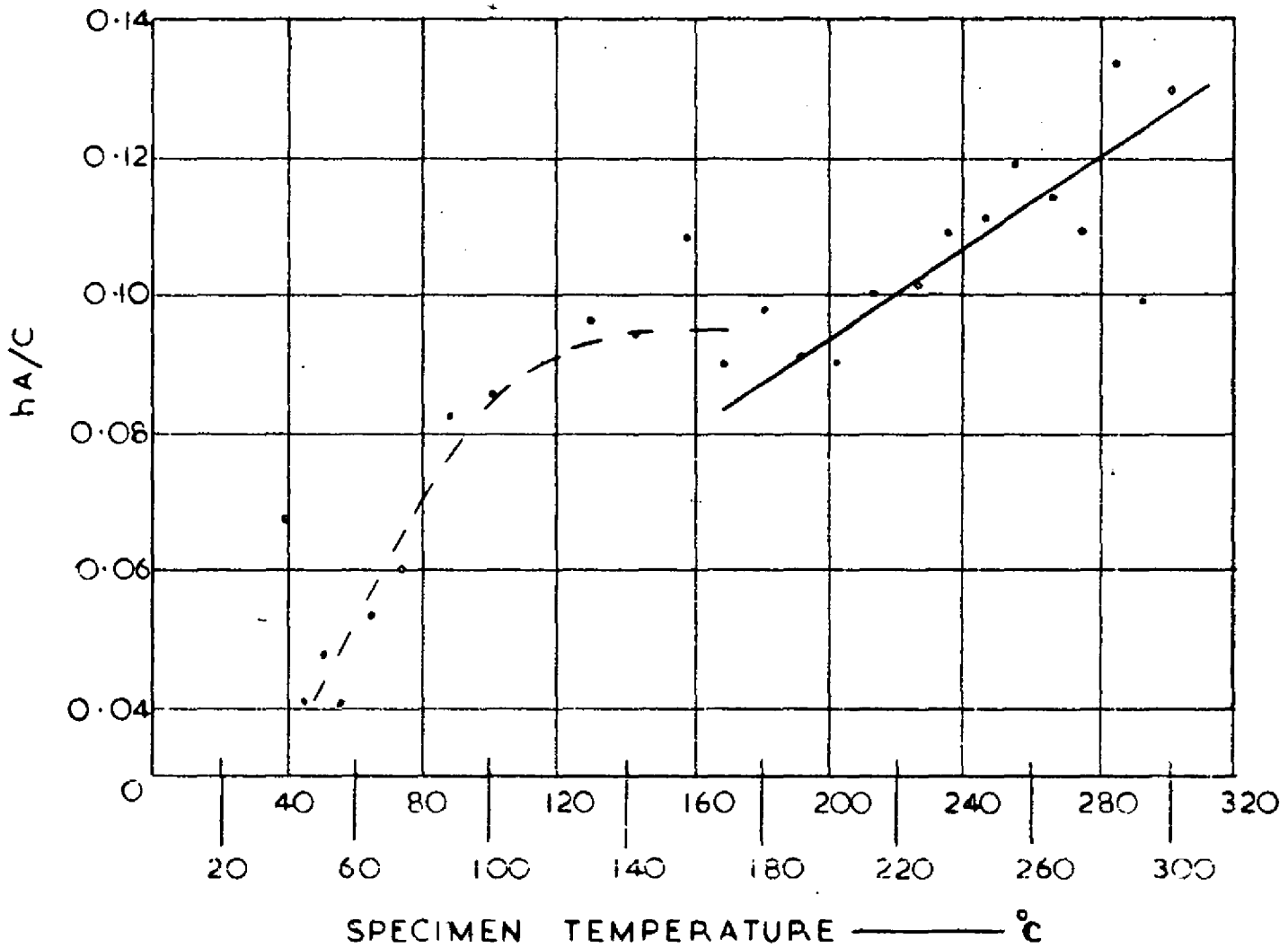
FIG.3. FACTOR hA/C FOR OAK
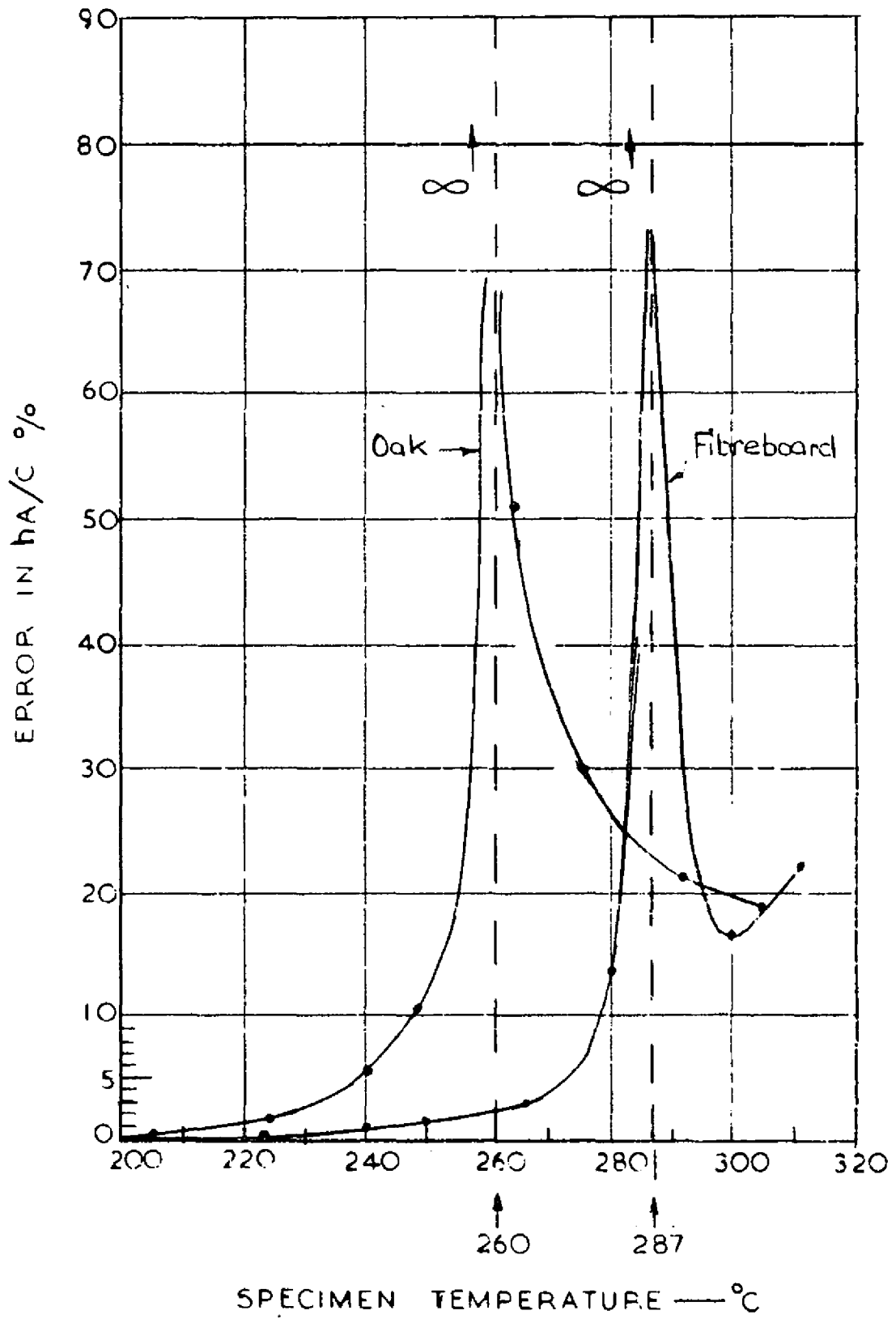
FIG.4. ERROR IN hA/C TO GIVE 1% ERROR IN q/c
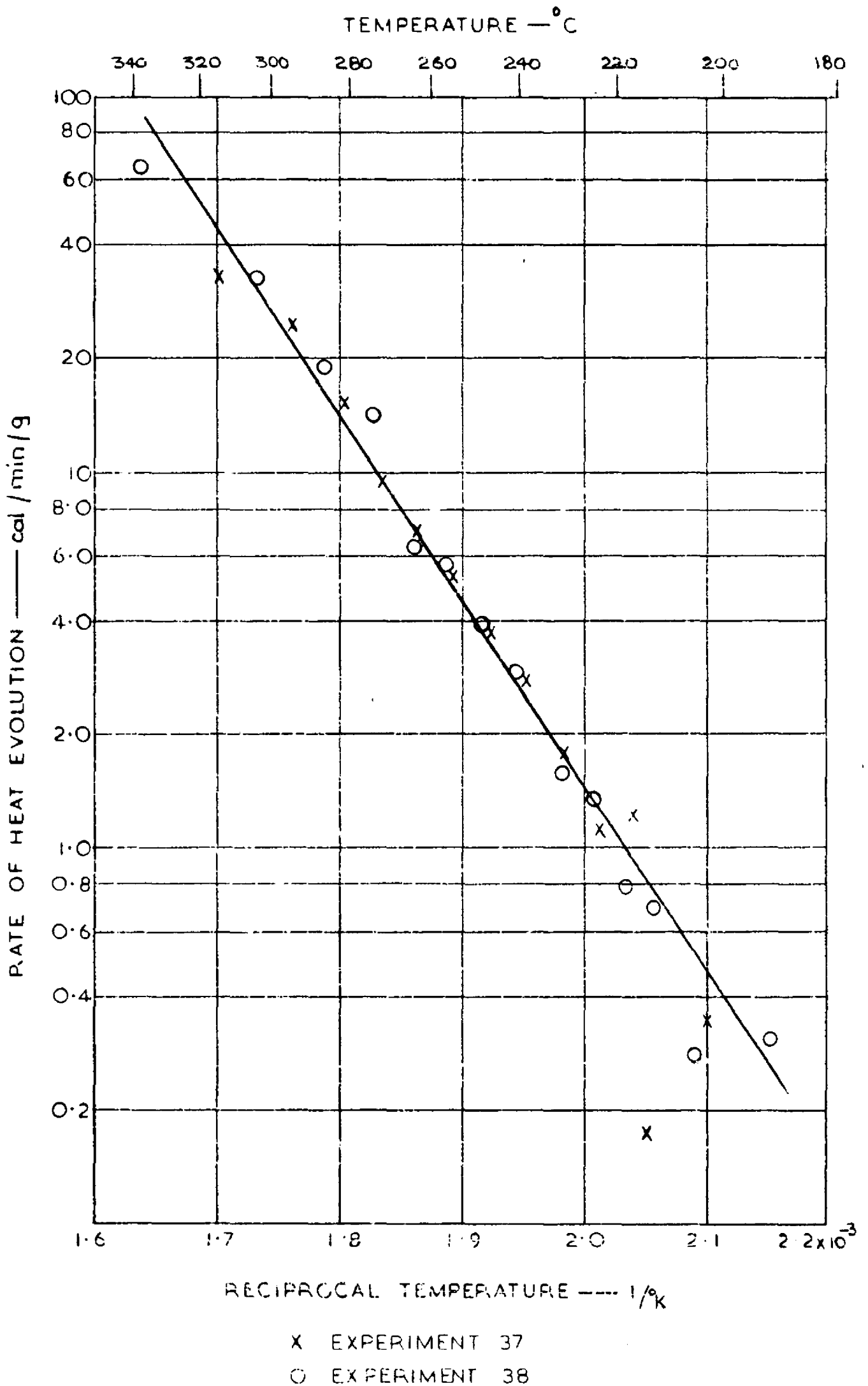
FIG 5. RATE OF HEAT EVOLUTION FOR OAK
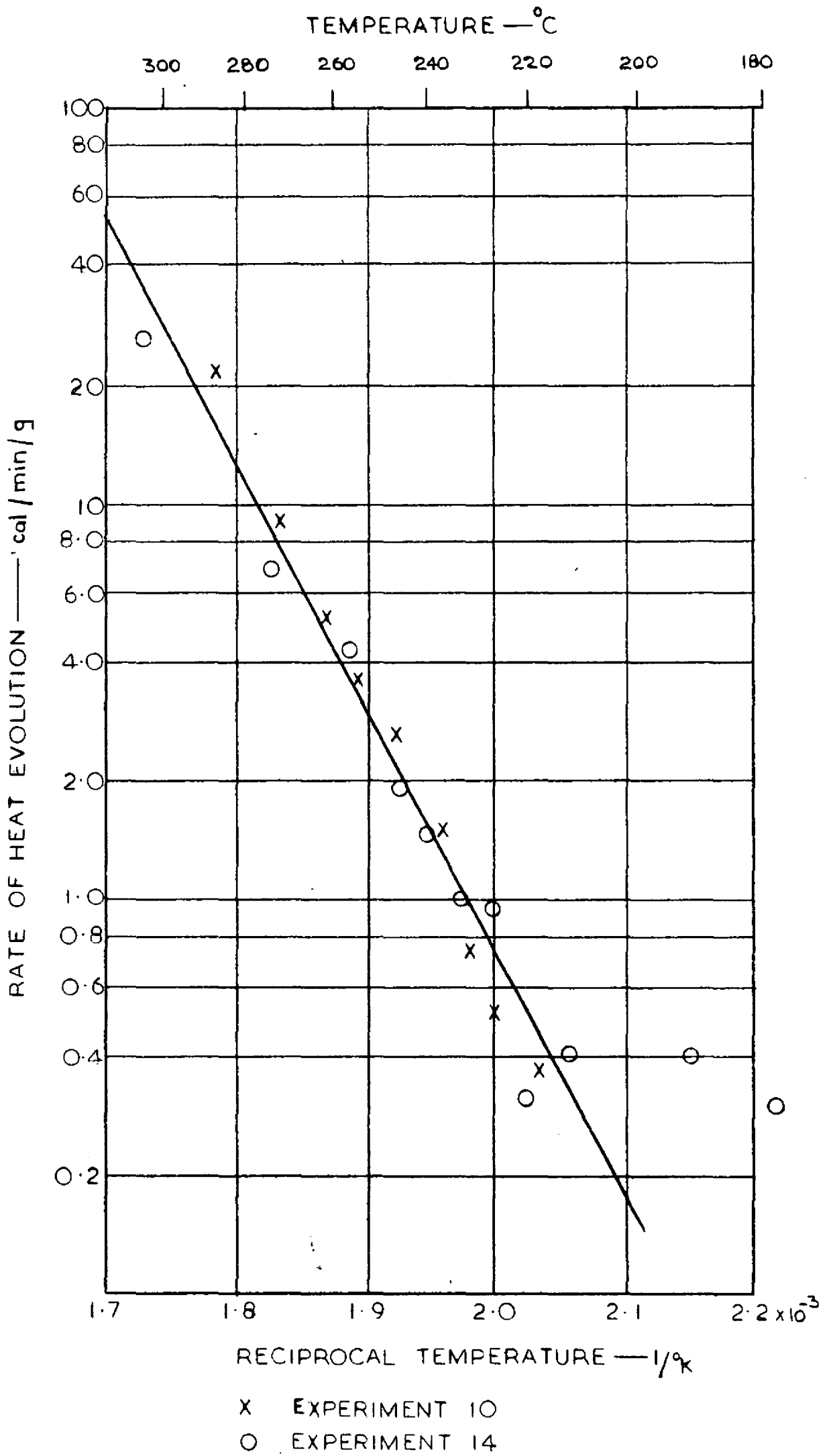
FIG. 6. RATE OF HEAT EVOLUTION FOR BEECH
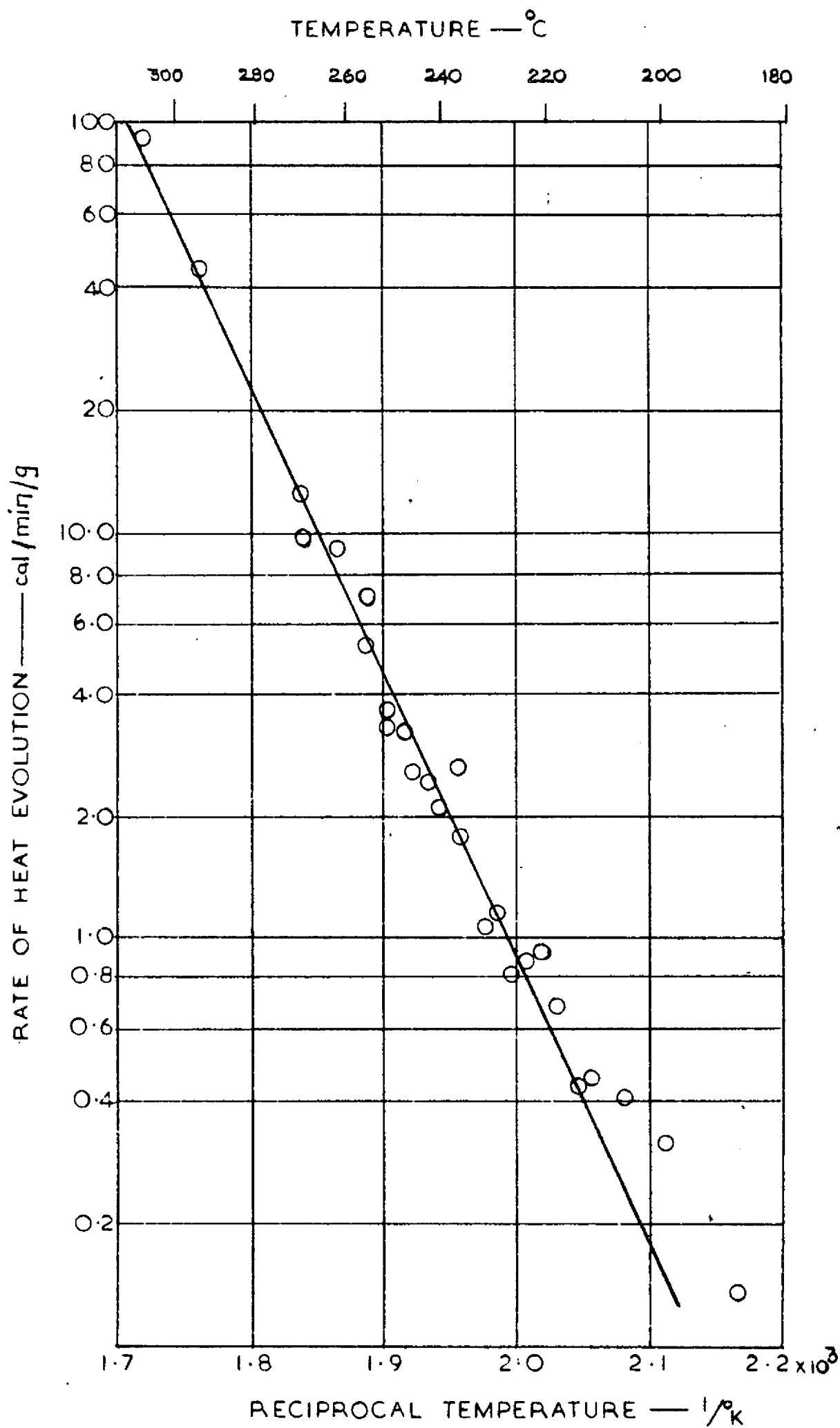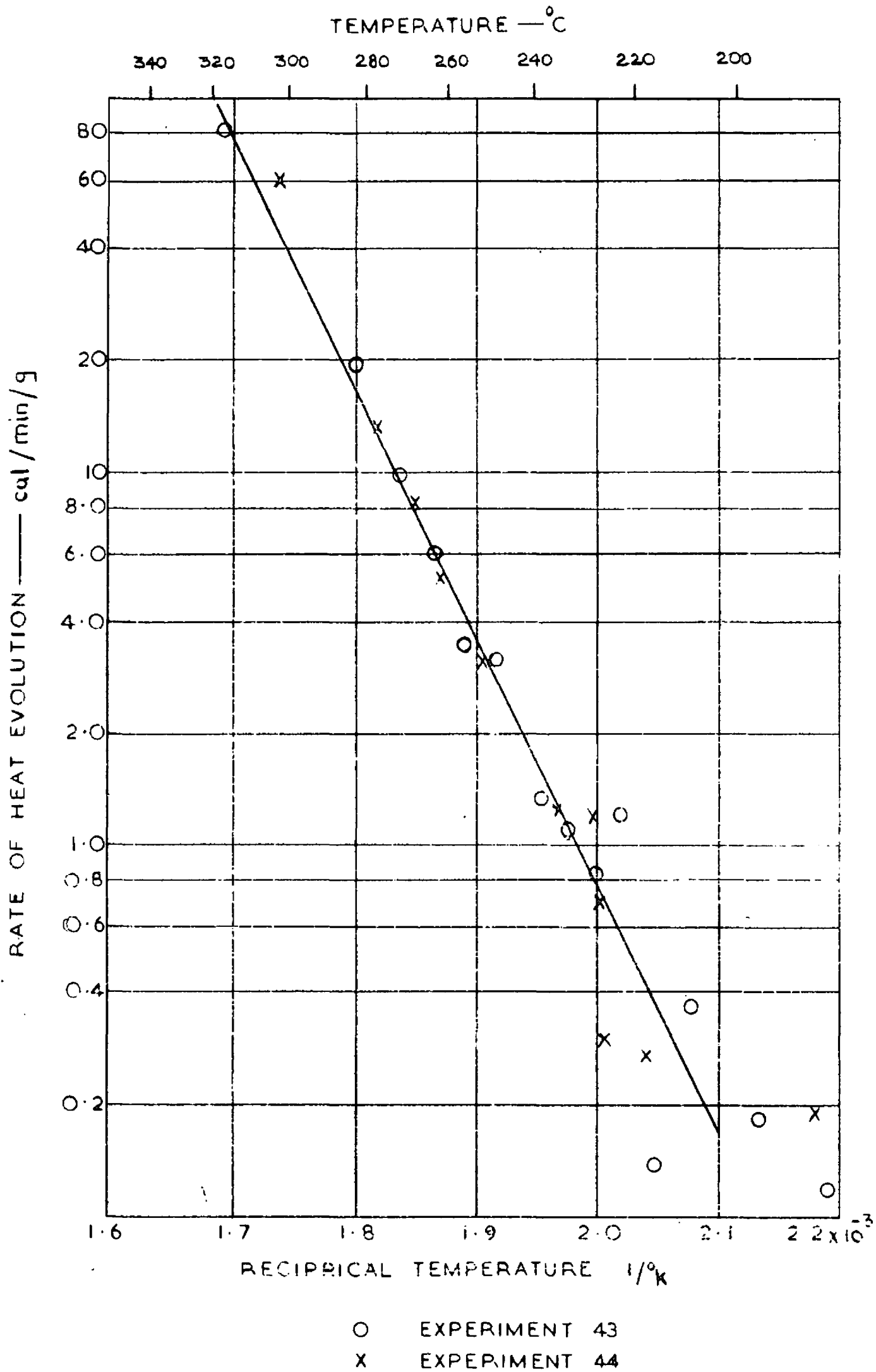
FIG. 7. RATE OF HEAT EVOLUTION FOR IROKO

EXPERIMENTS 33 & 34 COMBINED

FIG.8. RATE OF HEAT EVOLUTION FOR WESTERN RED CEDAR
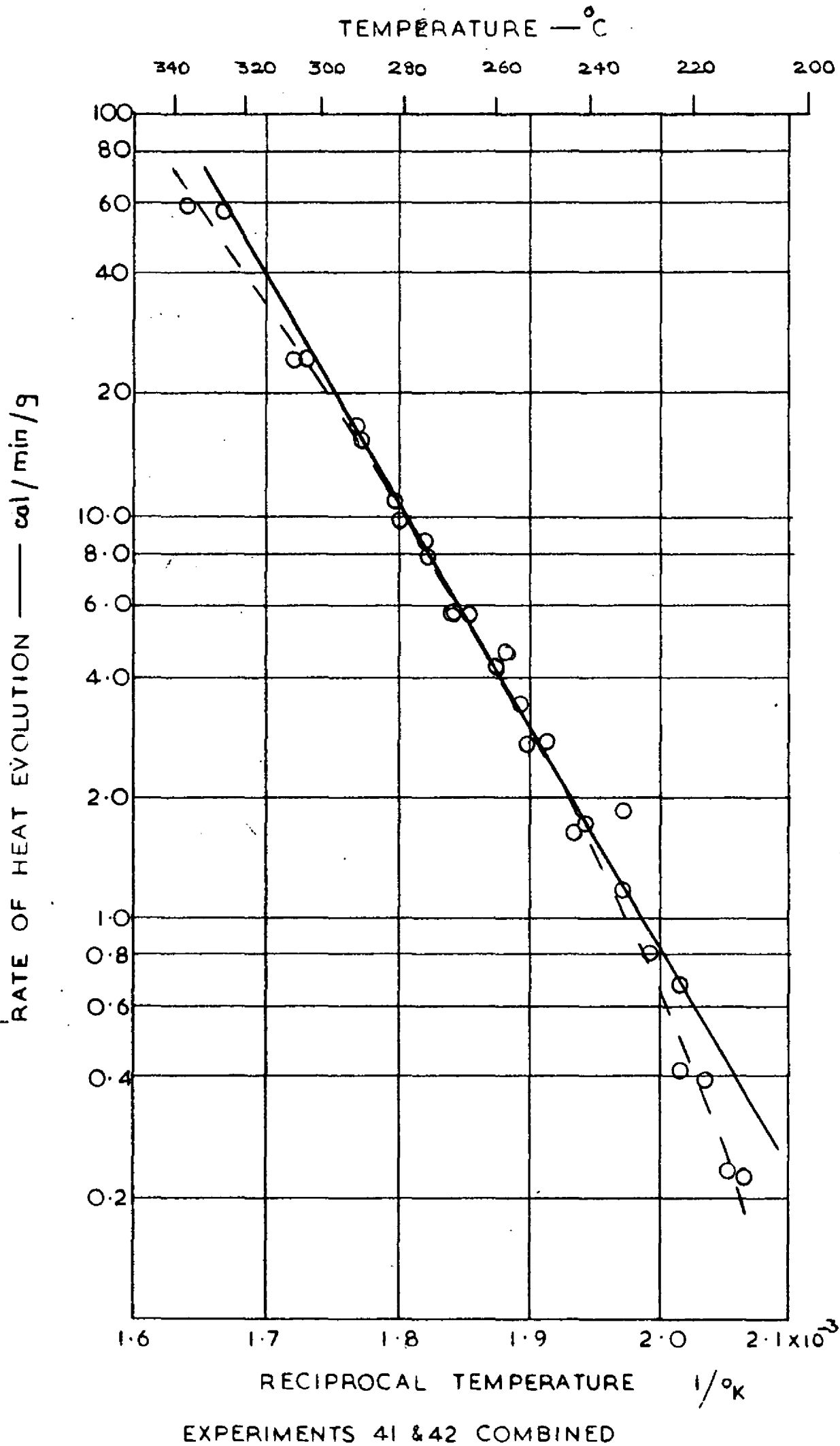
FIG. 9.   RATE OF HEAT EVOLUTION FOR
AMERICAN WHITEWOOD
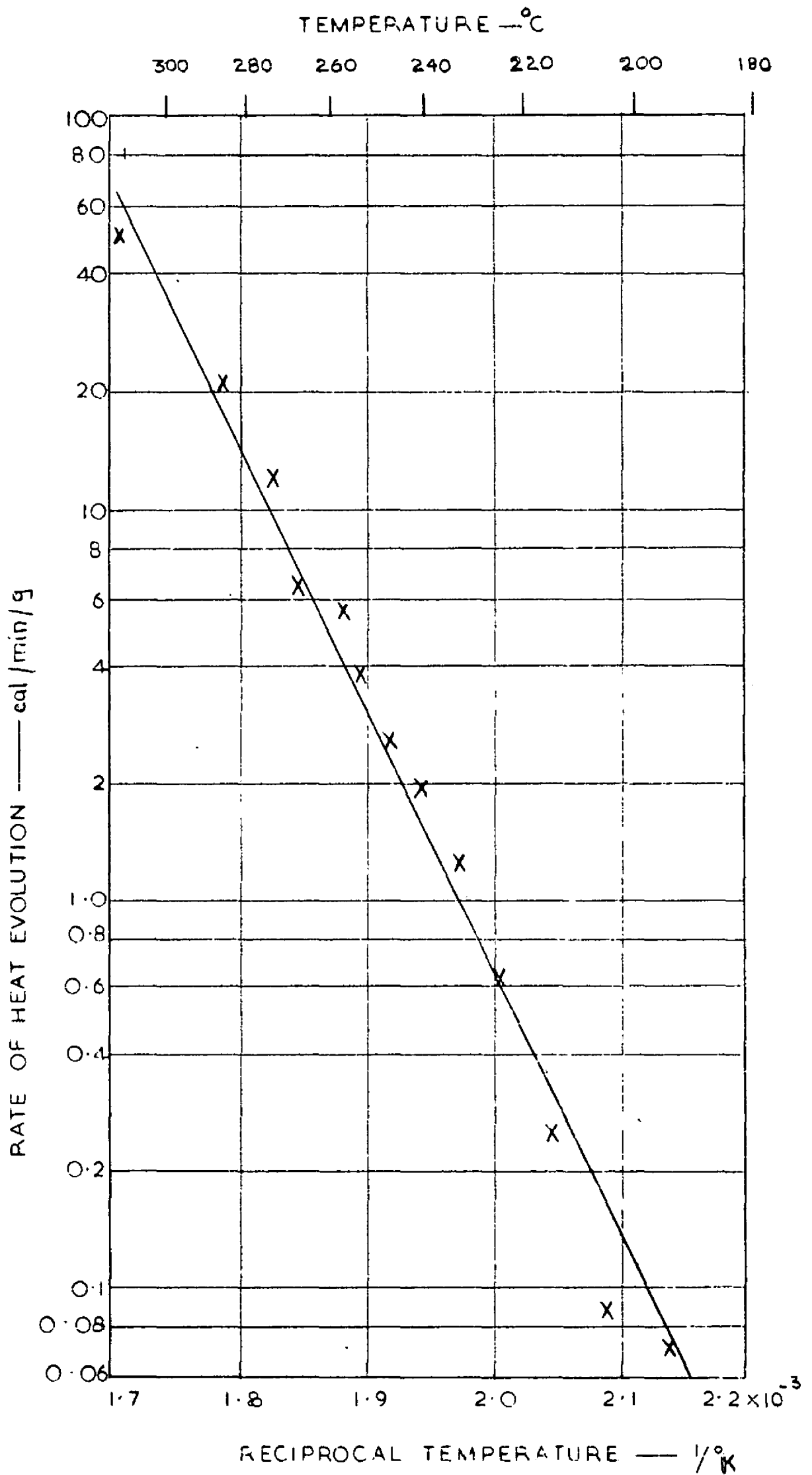
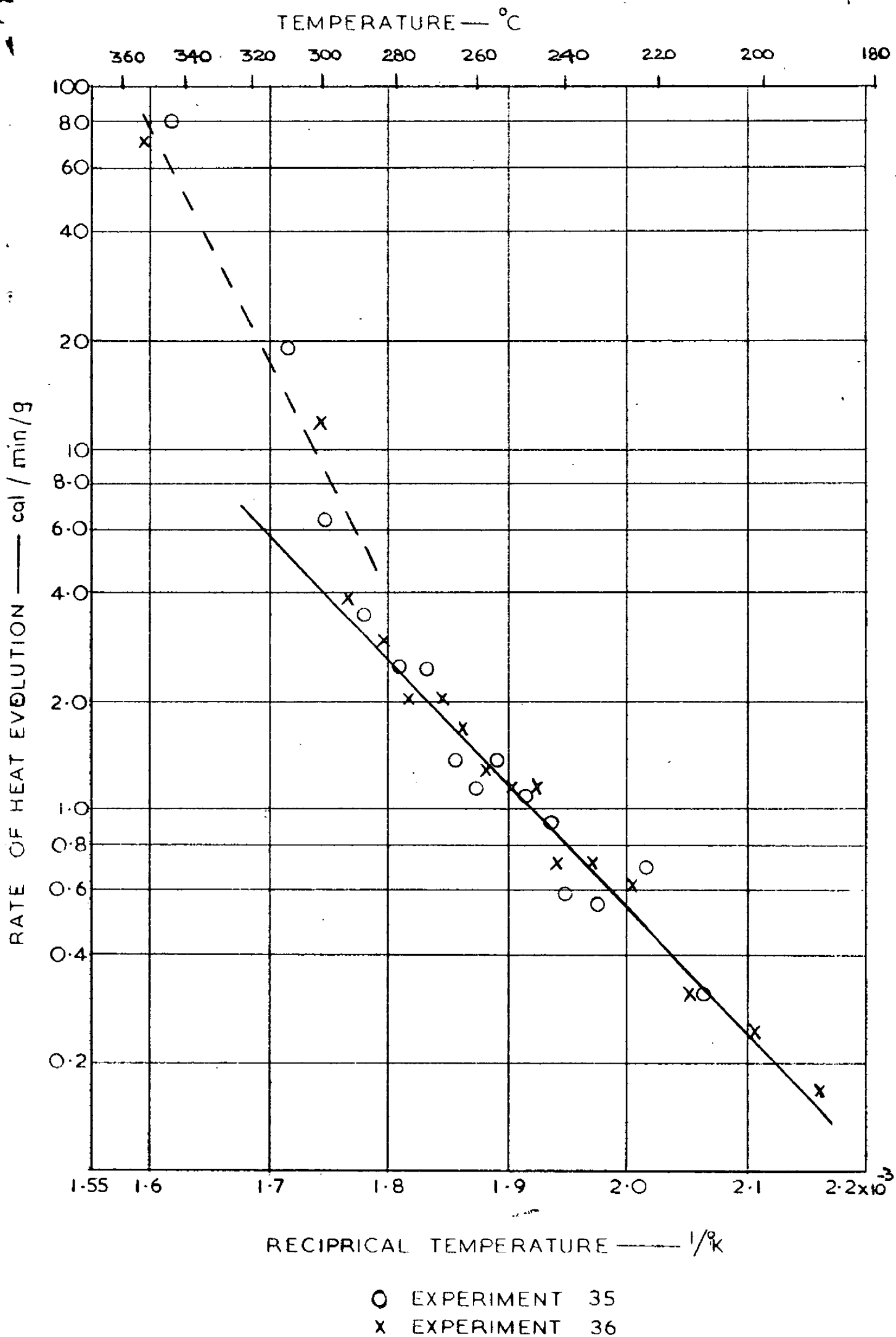FIG.10. RATE OF HEAT EVOLUTION FOR AFRICAN MAHOGANY   F.R.266. 1/2360

FIG 11 RATE OF HEAT EVOLUTION FOR
· FIBREBOARD