

THE MOVING BOAT TECHNIQUE AND PRACTICAL STUDIES ON THE DECOMPOSITION OF CARBONATES. PART 2. ANALYSIS AND PREDICTION OF $\alpha-t$ PLOTS GENERATED UNDER A NONLINEAR TEMPERATURE PROGRAMME

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ABSTRACT

Traditionally non-isothermal kinetic studies have been restricted to situations where the temperature rises continuously at a constant rate. The present work is concerned with the analysis and prediction of $\alpha-t$ plots when variation of temperature with time is arbitrary. Some actual experiments have been carried out using the moving boat technique and the kinetic data so generated analysed using the theory outlined.

It is shown that it may be possible to predict entire $\alpha-t$ plots using a numerical approach provided the temperature–time plot is known and suitable values of the kinetic parameters E and A are assumed. The kinetic parameters can be evaluated on the basis of some given α values for particular $T-t$ plots.

INTRODUCTION

Non-isothermal kinetic studies are of much practical relevance. They relate to both batch operations as well as continuous reactors. For example, an electric steelmaking furnace undergoes fluctuating temperature during a heat lasting, say, for several hours. In a sponge iron kiln, a lump of iron ore undergoes reduction from the input end to the final exit, the temperature fluctuating throughout. It is important to develop a theory by which it would be possible to predict the final degree of conversion for a given temperature–time history. Any such prediction necessarily requires the use of kinetic parameters which must be evaluated through test runs.

The progress of high temperature reactions depends on the nature of temperature variation and, therefore, it is very necessary to monitor temperature changes for proper process control. To obtain values of the operative kinetic parameters, samples of reacted mass are collected at different time intervals during a test run and they are analysed to obtain the respective α values. These values are then analysed to evaluate the kinetic parameters

with reference to the given $T-t$ plot. It is then possible to use these values in the prediction of $\alpha-t$ plots for arbitrary $T-t$ plots.

In the present case the theory proposed has been tested against some data on the decomposition of limestone which have been generated using the moving boat technique (MBT) described in Part 1 of this communication [1].

TEMPERATURE VARIATION IN MBT

Since this paper is concerned with the analysis of some data generated by MBT, the nature of temperature-time plots attainable in this technique is first discussed. As has been discussed in Part 1 of this communication [1], MBT employs a series of crucibles in a boat which enters a furnace at a steady speed. Volume elements of test sample contained in the crucible are exposed to the hot zone in the sequence of their arrangement, each individually undergoing the same temperature (T)-time (t) schedule but for varying intervals. The nature of the $T-t$ plot, which can be varied, depends on the speed of the boat, the temperature profile of the hot zone and the thermal properties of the sample. The equation defining the rate of temperature rise is derived as follows.

Suppose that the entire hot zone is at isothermal temperature T_f and a volume element enters the zone at any given speed. The volume element is heated by both radiative and convective heat flux. The rate of heating is given by the equation

$$\frac{dT}{dt} = K_1(T_f^4 - T^4) + K_2(T_f - T) \quad (1)$$

$$= [K_1(T_f^2 + T^2)(T_f + T) + K_2](T_f - T) \quad (2)$$

where K_1 and K_2 are constants and T is the temperature of the element. If $T \ll T_f$ or $T \approx T_f$ then eqn. (2) reduces to

$$\frac{dT}{dt} = q(T_f - T) \quad (3)$$

where q is a constant.

On integration one obtains

$$T = T_f - (T_f - T_0) \exp(-qt) \quad (4)$$

where T_0 is the initial temperature.

Equation (4) describes an exponential temperature rise which is obviously independent of the boat speed. In this case ($d \ln T / dt$) is constant rather than (dT / dt) as in TG.

The heating schedule is more complex when the furnace itself has a temperature profile. If it is assumed that T_f rises exponentially from the furnace mouth, then

$$T_f = T_m(1 - e^{-j'l}) \quad (5)$$

where T_m is the ultimate maximum temperature of the hot zone, j is a constant, and l the distance from the furnace mouth. If the speed of the boat is v then l equals vt . Incorporating eqn. (5) into eqn. (3) and integrating, one obtains an equation describing the variation of T with t

$$T = \frac{T_m}{q - jv} [q(1 - e^{jvt}) - jv(1 - e^{-qt})] \quad (6)$$

This indicates an S-shaped curve. That is, initially, when the volume is exposed to lower furnace temperatures, the heating rate is low. It gradually increases as the furnace temperature increases in the interior. Subsequently, as the volume element heats up and approaches T_m , the rate of heating drops. Equation (6) shows that the nature of $T-t$ plots can be changed by varying the boat speed and/or the furnace temperature profile.

It is possible to incorporate eqn. (4) or eqn. (6) into the non-isothermal kinetic equation for analysis of $\alpha-t$ plots generated under such heating schedules. However, the mathematics are cumbersome and the solution is not simple [2]. $\alpha-t$ plots can be more conveniently analysed and kinetic parameters evaluated by use of a graphical approach or a differential approach.

GRAPHICAL APPROACH

We have the basic equation

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^t \exp(-E/RT) dt \quad (7)$$

where $g(\alpha)$ and $f(\alpha)$ are appropriate functions. Consider a general situation where T varies with t arbitrarily. If it is assumed that the activation energy remains unchanged throughout then one can calculate the values of $\exp(-E/RT)$ at various values of t by considering the instantaneous values of temperature provided the value of E is known. The total area under the curve so obtained multiplied by A gives $g(\alpha)$. The value of A can be found from a suitable kinetic compensation plot or otherwise. To do the reverse, i.e., evaluate E from a known value of $g(\alpha)$, one should first use a set of E values to calculate $g(\alpha)$ values and then obtain the correct E value through a calibration procedure. The area calculations are conveniently done by using Simpson's one-third rule.

DIFFERENTIAL APPROACH

We have the well-known equation

$$\frac{d\alpha}{dt} = A \exp(-E/RT)f(\alpha) \quad (8)$$

$$\left(\frac{d\alpha}{dt}\right)/f(\alpha) = A \exp(-E/RT) \quad (9)$$

Now consider a general time-temperature variation

$$T = f_1(t) \quad (10)$$

$$\frac{dT}{dt} = f'_1(t) \quad (11)$$

where (dT/dt) varies with time. Now

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} f'_1(t) \quad (12)$$

combining eqn. (12) with eqn. (9) one obtains

$$\ln \left[\frac{d\alpha}{dT} f_1(t) / f(\alpha) \right] = \ln A - E/RT \quad (13)$$

Thus a plot of the left-hand side of eqn. (13) against reciprocal temperature would be linear and the slope and intercept would yield the values of E and A , respectively. If $\alpha-t$ and $T-t$ plots are established experimentally, then the left-hand side of eqn. (13) is evaluated easily provided the form of $f(\alpha)$ is known. The latter must be established through independent experiments. Once the kinetic parameters are evaluated, it should be possible to predict $\alpha-t$ plots for any other type of $T-t$ plot.

We shall now consider applications of these equations in analysing some kinetic data generated by MBT.

EXPERIMENTAL

Decomposition experiments were carried out using two limestone powder samples (2 and 3, described in Part 1 [1]) and a compact sample. The experimental set-up used was the same as described in ref. 1. Powder and lumpy compact samples were decomposed under several $T-t$ schedules under different combinations of boat speed and furnace temperature profile.

RESULTS AND DISCUSSION

As discussed in Part 1 [1], isothermal decomposition data obtained at three different temperatures could be fitted to the kinetic equation

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = 1 - (1 - \alpha)^{1/3} = kt \quad (14)$$

Therefore

$$f(\alpha) = 3(1 - \alpha)^{2/3} \quad (15)$$

This expression for $f(\alpha)$ is used in subsequent treatments.

Use of graphical integration

We first discuss the use of the graphical approach in analysing and predicting $\alpha-t$ plots. We start by noting that the E value for isothermal decomposition is 140 kJ mol^{-1} (33 kcal mol^{-1}). Suppose we assume this value of E in a non-isothermal case also. We then try to calculate A on the basis of a fixed point in the $\alpha-t$ plot and predict, on the basis of these E and A values, the entire $\alpha-t$ plot. The A value is determined according to eqn. (1) as

$$A = \frac{g(\alpha)}{\int_0^t \exp(-E/RT) dt} \quad (16)$$

Here the denominator is evaluated by Simpson's rule as mentioned earlier. $g(\alpha)$ is given by the equation established by isothermal experiments (eqn. 14).

Figure 1 shows an experimental $\alpha-t$ plot obtained under the temperature schedule shown. The figure also shows four $\alpha-t$ plots calculated on the basis

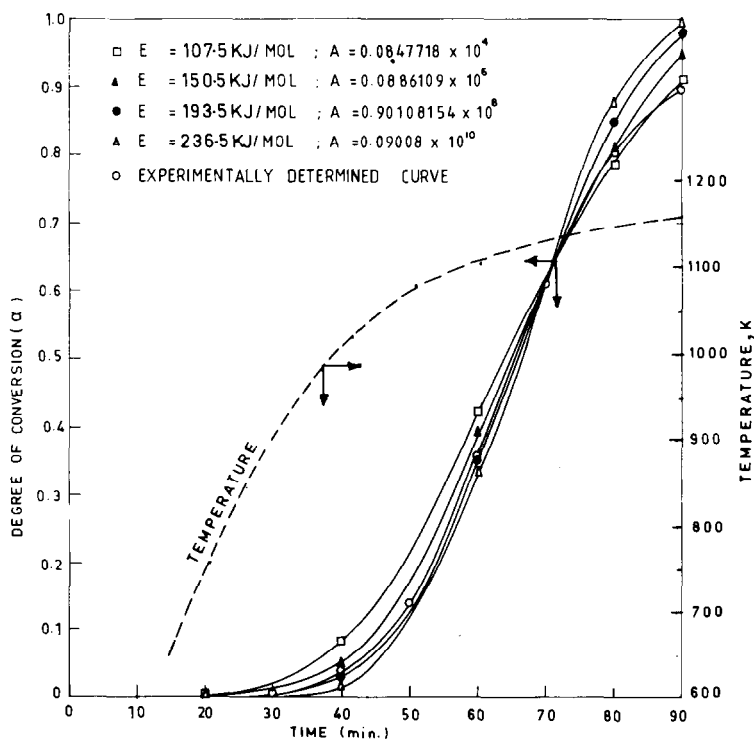


Fig. 1. Theoretical interpretation of $\alpha-t$ plots for different sets of E and A values using the single point determination of A at $t = 70 \text{ min.}$

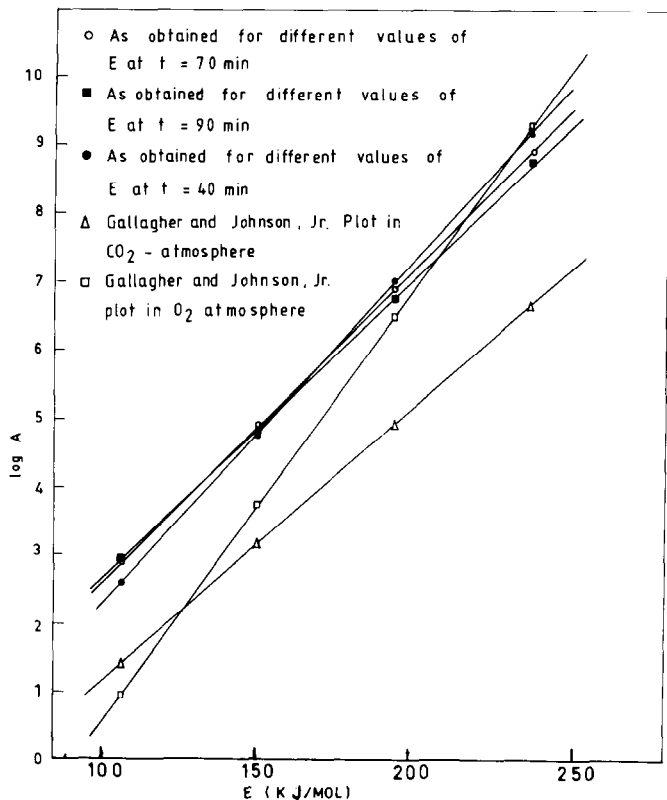


Fig. 2. Kinetic compensation plots.

of four assumed values of E in the range 107.5 – 236.5 kJ mol^{-1} and an α value for $t = 70$ min. These plots show that the correct E value perhaps lies between 150.5 and 193.5 kJ mol^{-1} . Similar single-point determinations of A and then calculations of α - t plots for $t = 90$ min and $t = 40$ min have been reported elsewhere [2]. These plots also confirm these values of E and A . The sets of assumed E and calculated A values conform to the kinetic compensation effect (KCE) as shown in Fig. 2. This figure also shows plots according to the KCE equations given by Gallagher and Johnson [3] for CaCO_3 decomposition in CO_2 and O_2 atmospheres.

Evaluation of kinetic parameters by the differential approach

In the previous section, we were concerned with the prediction of α - t plots for known T - t plots on the basis of assumed values of E . We will now discuss the reverse problem, i.e., how to evaluate E and A when the α - t plots as measured experimentally are available. For evaluation of the kinetic parameters we make use of eqns. (13) and (15).

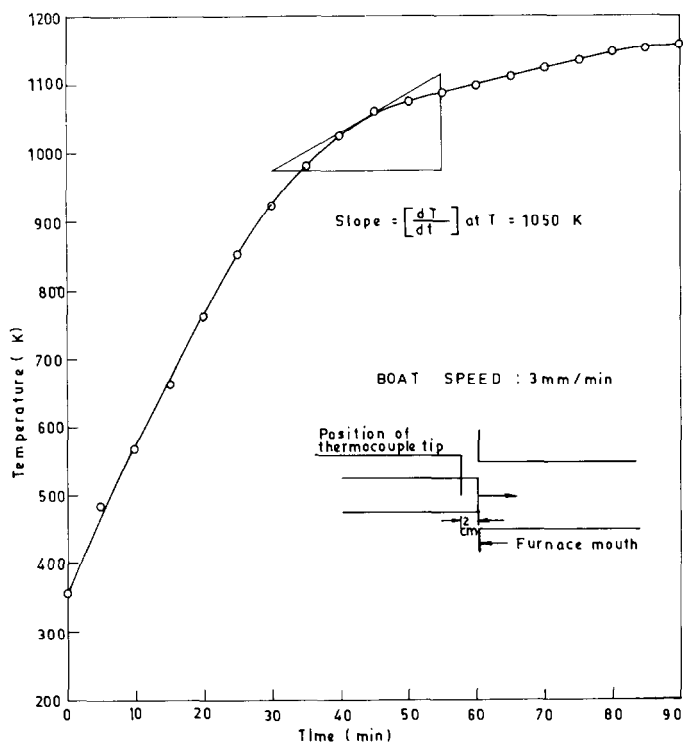


Fig. 3. Time temperature program obtained from MBT using a limestone sample (No. 2).

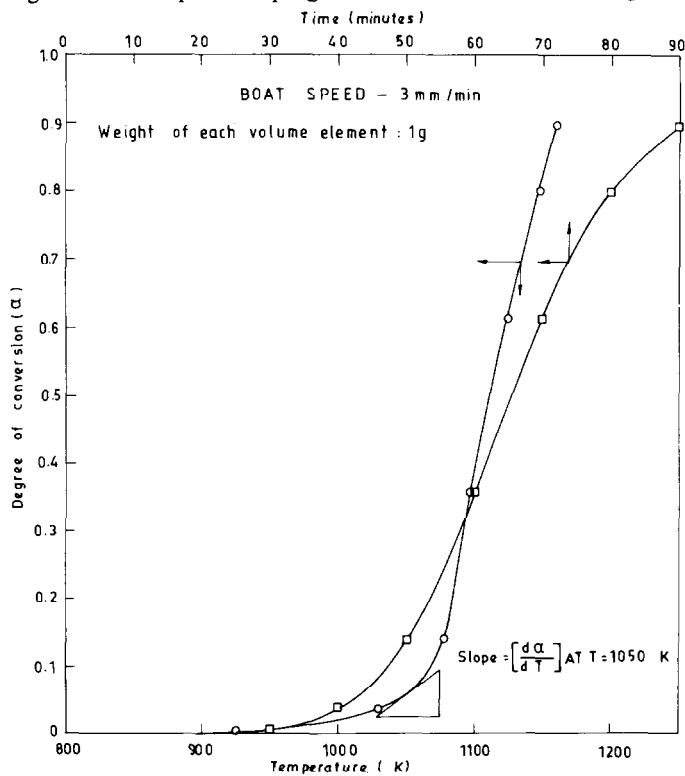


Fig. 4. Plots of $\alpha-t$ and $\alpha-T$ obtained from MBT using a limestone sample (No. 2).

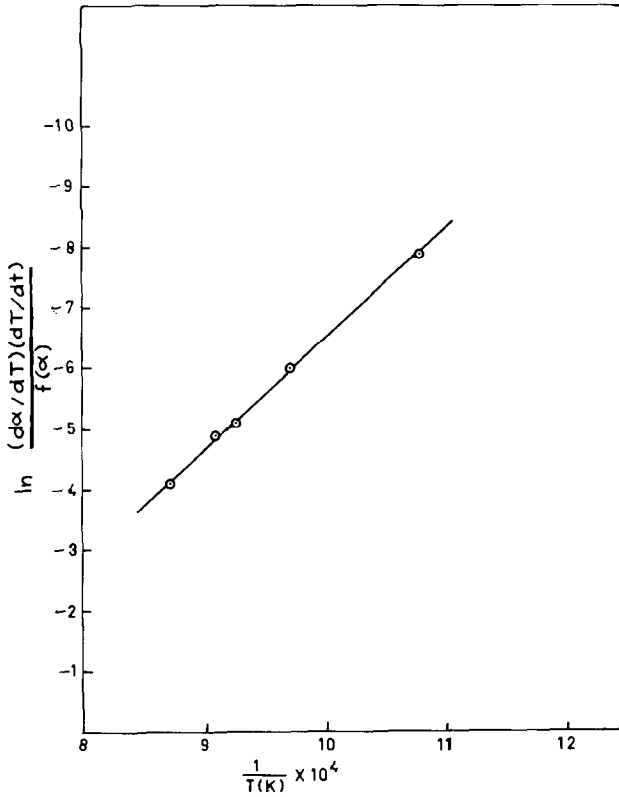


Fig. 5. Logarithmic plot of data shown in Fig. 4.

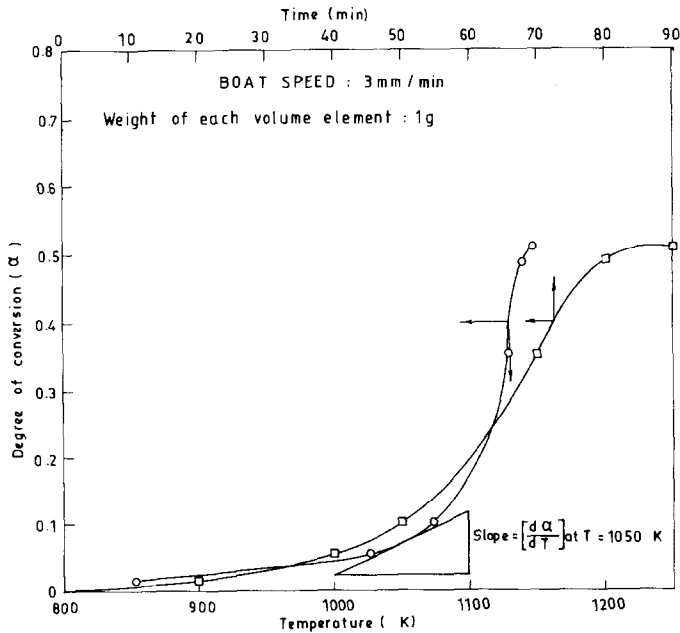


Fig. 6. Plots of $\alpha-t$ and $\alpha-T$ obtained from MBT using a limestone sample (No. 3).

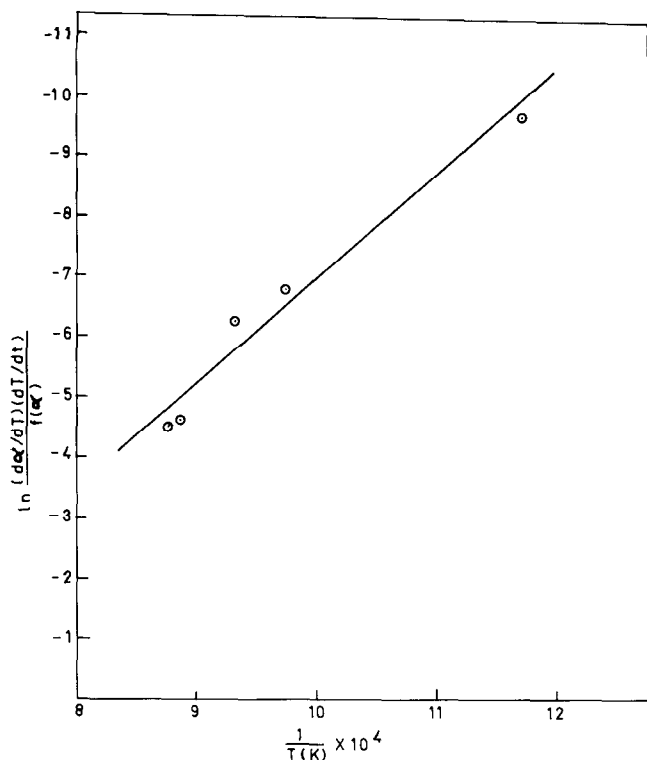


Fig. 7. Logarithmic plot of data shown in Fig. 6.

Figure 3 shows the temperature variation with time for a particular MBT run and Fig. 4 shows α values versus both time and temperature. Figure 5 shows a plot according to eqn. (13). The plot is linear and the slope and intercept have the values of 154 kJ mol^{-1} and 1.09×10^5 , respectively. It should be noted that since $(d\alpha/dT)/(dT/dt)$ equals $(d\alpha/dt)$, one can directly plot, using Fig. 4, values of $\ln(d\alpha/dt)/f(\alpha)$ against reciprocal temperature to get the same result.

Figure 6 shows $\alpha-t$ and $\alpha-T$ plots for a second sample and Fig. 7 shows the logarithmic plot. The latter, which is linear as expected, gives E and A values close to those given by Fig. 5. Two more plots for a third sample are shown in Figs. 8 and 9. All these sets are for different $T-t$ plots, yet they all lead to almost identical values of the kinetic parameters. We may, therefore, accept these values for the decomposition of loose powders irrespective of the $T-t$ schedule. The fundamental assumption then is this: no matter how temperature fluctuates there is a combination of E and A values which controls the changes in reaction rate during temperature fluctuations. The physical significance of these parameters is not clear. However, for a particular reaction mechanism, they have well-defined values which are not influenced by fluctuating temperature.

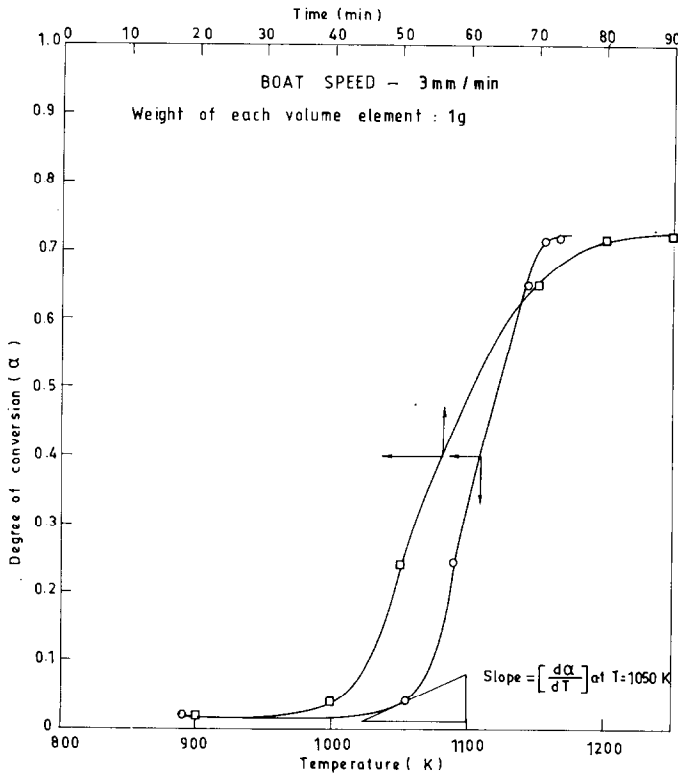


Fig. 8. Plots of $\alpha-t$ and $\alpha-T$ obtained from MBT using a limestone sample (No. 4).

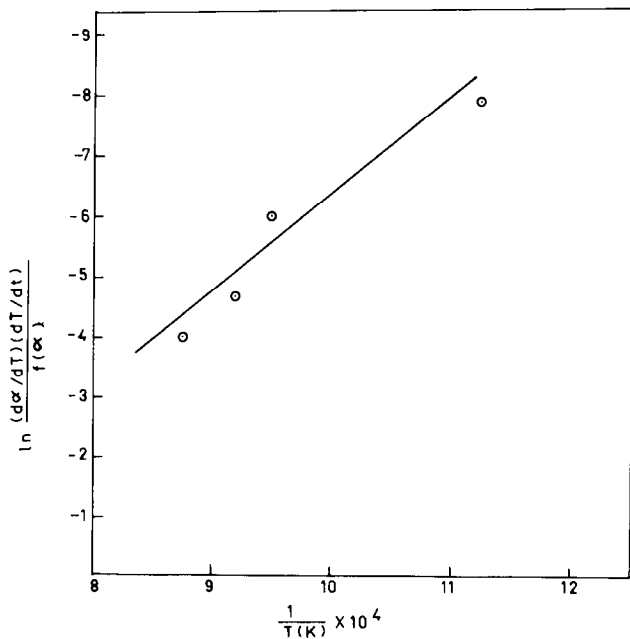


Fig. 9. Logarithmic plot of data shown in Fig. 8.

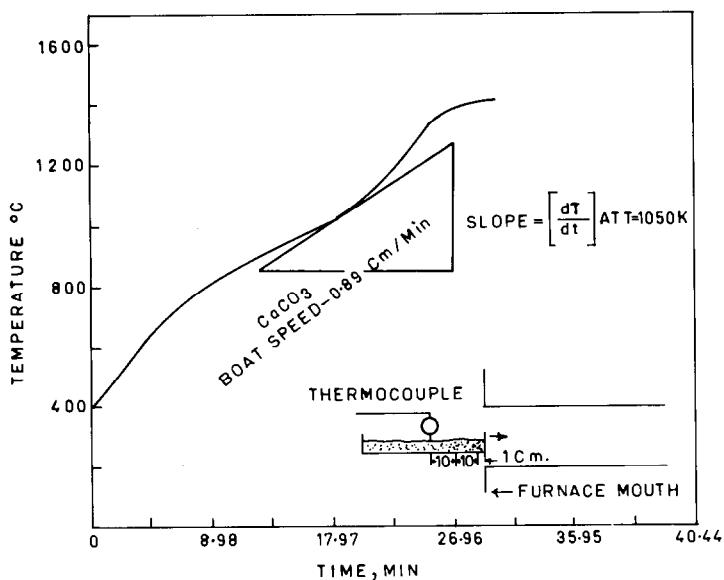


Fig. 10. $T-t$ plot for bulk packed bed of limestone.

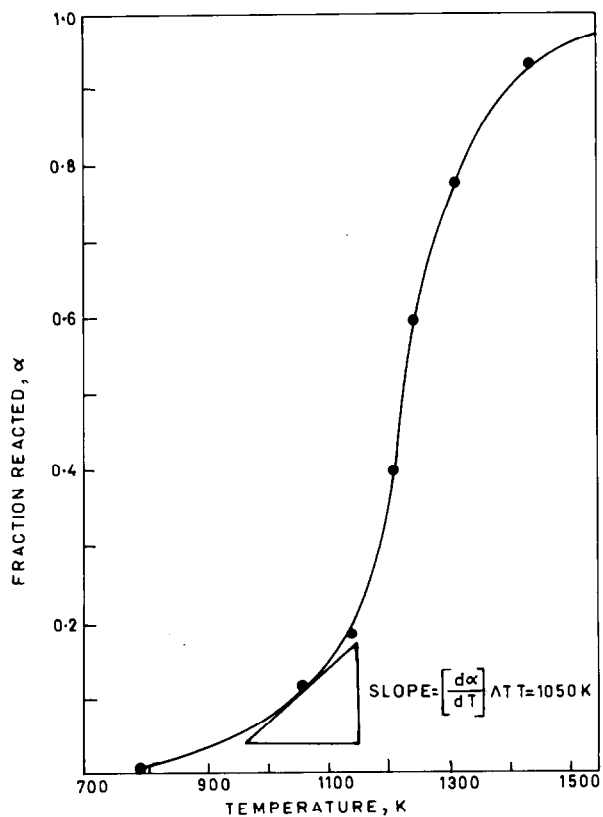


Fig. 11. $\alpha-T$ plot obtained from MBT using bulk limestone sample.

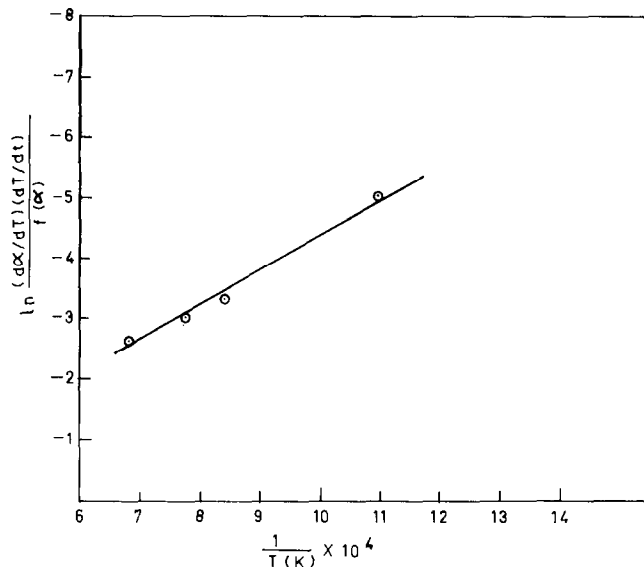


Fig. 12. Logarithmic plot for data shown in Fig. 11.

The kinetic parameters, however, will not remain unchanged when the reaction mechanism changes. For example, if CaCO_3 is taken in packed bulk form instead of as a limited quantity of loose powder, heat transfer to the sample interior becomes difficult and the endothermic decomposition reaction tends to cool the interior. The reaction may then become heat transfer controlled. Figure 10 shows the $T-t$ plot for a packed bed of limestone. The intermediate dip in the temperature plot is obviously due to absorption of heat and consequent lowering of the rate of temperature rise because of onset of endothermic decomposition. Obviously heat transfer plays an important role here. Figure 11 shows the $\alpha-t$ plot which was established by taking small weighed samples from different locations in the boat and determining maximum weight loss on further heating. The logarithmic plot shown in Fig. 12 indicates a rather small value of E ($\sim 40 \text{ kJ mol}^{-1}$) which is consistent with heat transfer control. However, the plot suffers from one uncertainty, i.e., the form of $f(\alpha)$ assumed is identical to those taken earlier. This may not be valid in this case.

CONCLUSIONS

It may be concluded that a numerical approach can be used to predict $\alpha-t$ plots for a general heating schedule provided the appropriate values of the kinetic parameters are known. The latter may be evaluated by using some control experiments where both $\alpha-t$ plots are experimentally determined for known $T-t$ plots. It seems that a chosen set of E and A values

does not change with changes in heating schedule and, therefore, results obtained from controlled experiments can be extended to situations where temperature fluctuations are arbitrary.

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