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USE OF RECIPROCAL TEMPERATURE RISE EQUATION IN ANALYSIS OF NON-ISOTHERMAL KINETIC DATA IN GENERAL

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ABSTRACT

Theoretical analysis of kinetic data obtained under increasing temperature conditions requires the solution of an exponential integral through various approximations. This paper shows that some common types of temperature variation approximating linear variation can be described, at least in limited temperature ranges, by a reciprocal temperature rise equation of the kind

$$\frac{1}{T}=a-bt$$

where T is the absolute temperature, t is time and a and b are constants. Use of this equation leads directly to a simple and exact solution. A set of actual experimental data on the decomposition of $CaCO_3$ is analyzed to substantiate the approach proposed and demonstrate its usefulness.

INTRODUCTION

Theoretical analysis of kinetic data obtained under increasing temperature conditions rests on the combination of three basic equations which describe the following.

(a) The kinetic law

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k\,\mathrm{f}(\alpha) \tag{1}$$

where α is the fraction of reaction completed in time t, k is the temperature dependent rate constant, and $\mathrm{f}(\alpha)$ is a function of α whose appropriate form depends on the reaction mechanism.

(b) The so-called Arrhenius type expression to describe the variation of rate constant with temperature T

$$k=A\exp(-E/RT) \tag{2}$$

where A is a pre-exponential constant, R is the universal gas constant, and E is the activation energy.

(c) Equation describing variation of temperature with time

$$T = f'(t) \tag{3}$$

Thermogravimetry (TG) is generally carried out with a constant heating rate. If the heating rate is B, then eqn. (3) is written as

$$T = T_0 + Bt \tag{4}$$

where T_0 is the initial temperature at zero time and T is the temperature at time t.

Equations (1), (2) and (4) can be combined to give the basic equation for treatment of TG data

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{B}\int_0^T \exp(-E/RT)\, dT \tag{5}$$

This exponential integral is not amenable to analytical solution and, therefore, only approximate solutions based on various approximations are possible. A good deal of the literature on the subject centres around evaluation of this integral which becomes more complicated if the heating rate B is not constant, i.e. if temperature variation is non-linear.

Coats and Redfern [1] have given the following approximate solution for heating under constant rate

$$g(\alpha) = \frac{ART^2}{BE}\, e^{-E/RT}\left[1 - \frac{2RT}{E}\right] \tag{6}$$

If $f(\alpha)$ has a form $(1-\alpha)^n$ and if $n \neq 1$, then

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \ln \frac{AR}{BE}\left[1 - \frac{2RT}{E}\right] - \frac{E}{RT} \tag{7}$$

It is, therefore, possible to obtain approximate linear plots by plotting the left-hand side of eqn. (7) against the reciprocal temperature and then obtain E from the slope. In another approach proposed by Ingraham [2] $\ln(B\alpha/T^3)$ is plotted against $1/T$ to give a slope of E/R. In the literature there are many other similar relationships which have been proposed from time to time.

A SPECIAL TIME-TEMPERATURE PROGRAMME

A special case arises if the temperature variation is given by the equation

$$\frac{1}{T} = a - bt;\ d(1/T) = -b\, dt \tag{8}$$

where a and b are constants. Combining eqn. (8) with eqns. (1) and (2) one gets the simple and exact result

$$\ln g(\alpha) = \ln(AR/bE) - E/RT \tag{9}$$

This paper shows that under certain conditions eqn. (8) can approximately describe temperature variation of the linear as well as some other forms if values of a and b

are chosen appropriately. Therefore, eqn. (9) can be employed to analyze kinetic data.

CONVERSION OF LINEAR TEMPERATURE RISE EQUATION TO RECIPROCAL TEMPERATURE RISE EQUATION

Equation (4) may be written as

$$\frac{1}{T}=\frac{1}{T_0(1+Bt/T_0)}=\frac{1}{T_0}\left(1-\frac{Bt}{T_0}\right)=\frac{1}{T_0}-\frac{Bt}{T_0^2} \qquad (10)$$

provided that $Bt/T_0 \ll 1$. Thus, if the non-isothermal range of reaction (Bt) is small compared to the initial temperature, then eqn. (4) can be written in the form of eqn. (8) where a equals $1/T_0$ and b equals B/T_0^2.

Matching of the actual data to the reciprocal temperature rise equation is described next and it is shown that this is easier when the heating rate is not entirely constant but increases slightly with time as is found in some commercially available equipment.

MATCHING OF DATA

Suppose that the linear temperature (K) rise equation is

$T=600+20\,t$

i.e., $T_0=600$ and $B=20$. If t is in minutes, then the heating rate is 20°C min^{-1}. Let us also assume that we wish to describe the temperature data in the range 900–1100 K by a reciprocal temperature rise equation.

If we shift $t=0$ to 900 K then new values of T_0 and B are 900 (T_0') and 20, respectively. Thus if we assume eqn. (8) to be valid then a (i.e. $1/T_0'$) equals $1/900$ and b (i.e. $B/T_0'^2$) equals $20/(900)^2$. The temperatures obtained by using these values of a and b in the equation $1/T=a-bt$ are shown in Fig. 1. As expected, the new plot shows a gradual deviation from the linear plot at higher values of t. A better matching can be obtained by changing the value of b using a slightly lower value of B. A plot obtained by using $B=17.5$ and, therefore, $b=17.5/(900)^2$, is also shown in Fig. 1. Obviously, better matching can be obtained if T_0 is set at a value higher than 900 K. We may thus conclude that it is possible to approximately fit the linear data into a reciprocal temperature rise equation provided T_0 is high and the temperature range under consideration is small. A similar suggestion has been made by Akita and Kase [3].

It should be emphasized at this point that for arriving at the result [eqn. (9)] and the evaluation of the activation energy it is not always necessary to know the exact values of a and b. It is sufficient to establish the constraint $Bt/T_0 \ll 1$ and, therefore, ensure that there is a suitable equation. It is interesting to note that Satava [4], using an entirely different approach, has shown that, for the correct mechanism, log g(α) must be a linear function of $1/T$.

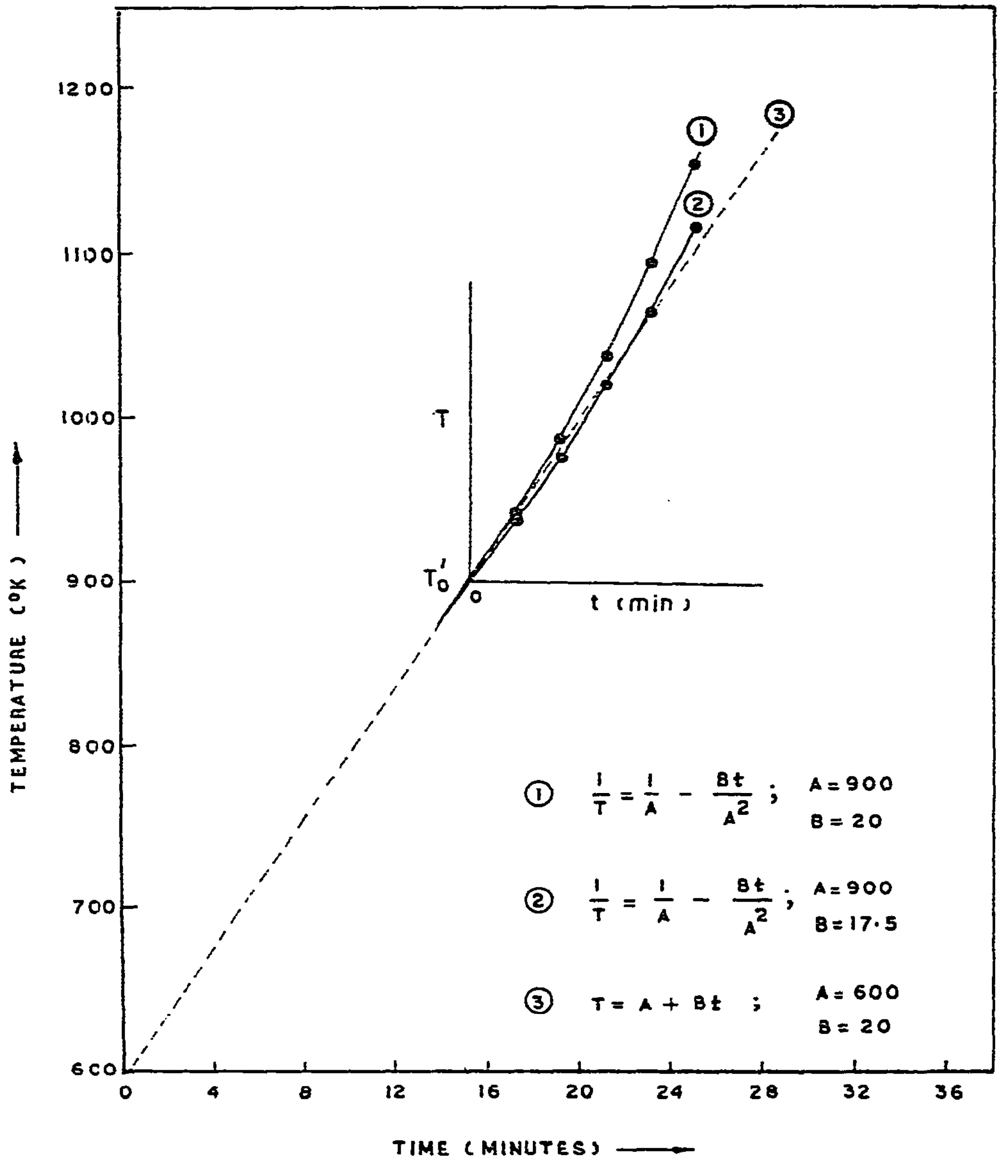

Fig. 1. Matching of the reciprocal temperature rise equation with constant rate of rise equation.

ANALYSIS OF TYPICAL EXPERIMENTAL DATA

Figure 2 shows some typical data for the decomposition of calcium carbonate various conditions. These data were obtained using a Stanton-Redcroft thermobalance (model TG-770) which allowed linear temperature rise at variable rates and flushing of the system with gas, if necessary. The $CaCO_3$ used was −200 mesh Ben Bennet limestone of composition CaO, 99.5–99.8%; MgO, 0.1–0.2%; SiO_2, 0.1–0.2% and Fe_2O_3, 0.1–0.2%. The gases used (N_2 and CO) were obtained directly from the

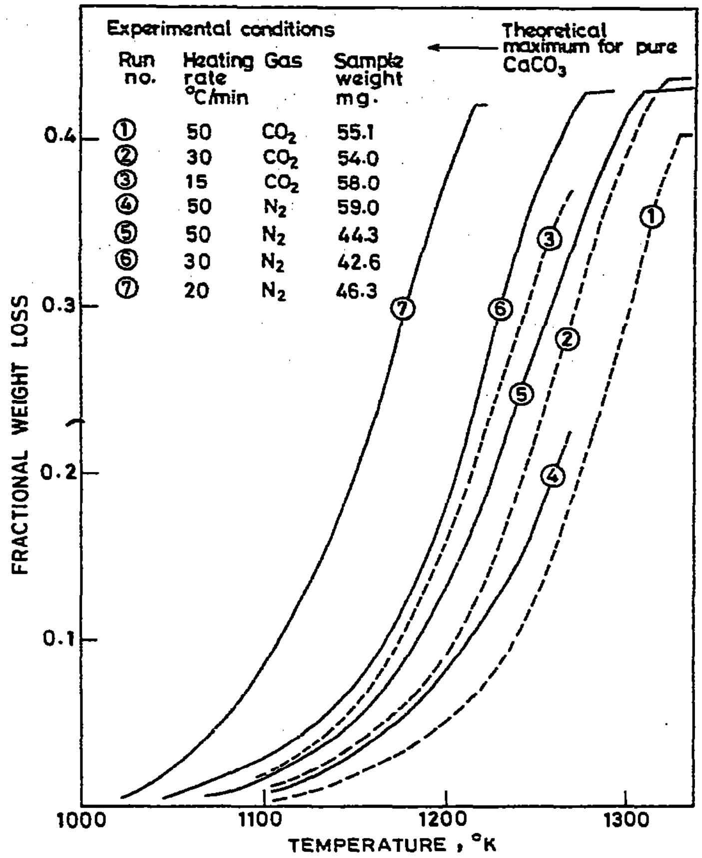

Fig. 2. TG data for the non-isothermal decomposition of calcium carbonate.

TABLE 1

Results of analysis of non-isothermal decomposition data by various methods: calculation of activation energy, E (kcal mole^{-1})
$g(\alpha) = 1-(1-\alpha)^{1/3}$

Run no.	Coats and Redfern			Ingraham			Present method		
	Corr. coeff.	Slope	E	Corr. coeff.	Slope	E	Corr. coeff.	Slope	E
1	0.9977	26786	53.6	0.9970	24933	49.9	0.9960	29564	59.1
2	0.9947	23842	47.7	0.9924	21379	42.8	0.9954	25904	51.8
3	0.9977	25027	50.1	0.9972	22296	44.6	0.9982	26960	53.9
4	0.9962	24738	49.5	0.9956	22884	45.8	0.9964	26805	53.61
5	0.9956	25854	51.7	0.9941	23715	47.4	0.9959	28136	56.3
6	0.9972	23753	47.5	0.9960	21503	43.0	0.9970	26066	52.2
7	0.9945	20159	40.3	0.9910	17589	35.2	0.9950	22359	44.7

cylinder at a flow rate of approximately 10 ml min^{-1}. Other experimental conditions are indicated in the figure.

The data shown in Fig. 2 have been analyzed using the methods proposed by Coats and Redfern [1] and Ingraham [2] and also by the method proposed in this paper. Table 1 shows the results of calculations in terms of correlation coefficients for the linear plots proposed, slope and the activation energy values obtained.

The values obtained using the method proposed are on the higher side although the variations amongst the data are similar. It is seen that a simple plot of ln $g(\alpha)$ vs. $1/T$ gives a linear plot, the slope of which gives the activation energy. It is known that, in general, the value of the activation energy obtained from the analysis of non-isothermal kinetic data varies with the method of analysis employed. Thus, the values obtained using the simple approach suggested here are perhaps no less reliable.

CONCLUSION

It is shown that if the rate of heating is constant during increasing temperature experiments, then the temperature variation can also be described approximately by the reciprocal temperature rise equation, provided the temperature range being considered is limited and the initial temperature being considered is high. The use of the reciprocal temperature rise equation affords a simple method of analyzing non-isothermal kinetic data.

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