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THERMAL DECOMPOSITION OF $MnCO_3$ (IN AIR)

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ABSTRACT

Both isothermal and non-isothermal studies have been used to investigate the kinetics of thermal decomposition of $MnCO_3$.

From equilibrium weight loss at different temperatures, the chemical mechanism was revealed. The mechanism of decomposition and rate-controlling step were determined. Then, the activation energy was calculated in each case using a newly proposed technique.

THEORETICAL TREATMENT OF THERMAL CURVES

A new method is proposed that enables calculation of the activation energy, E, from combined thermogravimetry (TG) and differential thermogravimetry (DTG) curves and so does not involve errors arising from numerical differentiation of TG data.

Consider the generalized kinetic equation

$$\frac{dw}{dt} = Ae^{-E/RT}f(w)$$

where w = unreacted weight at any time t, A = frequency factor, T = temperature (K). If $f(w)$ can be written as w^n, then we get

$$\frac{dw}{dt} = Ae^{-E/RT}w^n \qquad (1)$$

This will be the case when phase boundary motion controls ($n = 1/2$ or $2/3$) or if homogeneous nucleation takes place ($n = 1$ in first-order kinetics) or if the reaction is eventually of zero order [1–3].

Considering Fig. 1 where corresponding TG and DTG plots are shown. Points 1 and 2 on the DTG trace have the same dw/dt values corresponding to weights w_1 and w_2 on the TG trace.

Hence, substituting in eqn. (1)

$$\left(\frac{dw}{dt}\right)_1 = Ae^{-E/RT_1}w_1^n$$

$$\left(\frac{dw}{dt}\right)_2 = Ae^{-E/RT_2}w_2^n$$

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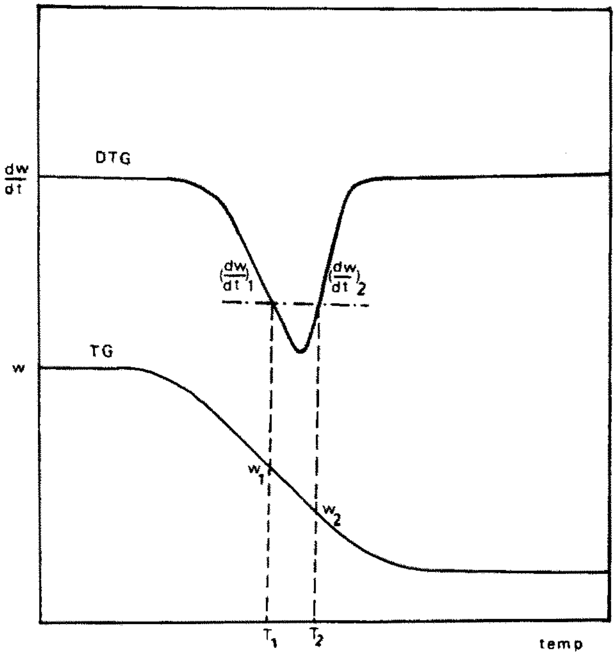

Fig. 1. Typical TG and DTA curves for a decomposition reaction.

Since $(\mathrm{d}w/\mathrm{d}t)_1 = (\mathrm{d}w/\mathrm{d}t)_2$, then

$$Ae^{-E/RT_1}w_1^n = Ae^{-E/RT_2}w_2^n$$

or

$$\exp\left[-\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right] = \left(\frac{w_2}{w_1}\right)^n$$

or

$$\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = n\ \ln\left(\frac{w_1}{w_2}\right)$$

or

$$\lambda = \frac{E}{n} = \frac{R\ \ln w_1/w_2}{\dfrac{1}{T_2}-\dfrac{1}{T_2}} \qquad (2)$$

The value of λ should be constant for any two points on the DTG trace having equal values of $\mathrm{d}w/\mathrm{d}t$ regardless of their locations.

Once the value of λ is known, then we set $E = \lambda n$. Replacing in eqn. (1) we get

$$\frac{\mathrm{d}w}{\mathrm{d}t} = Ae^{-n\lambda/RT}w^n$$

or

$$\ln\frac{dw}{dt} = \ln A + n\left(\ln w - \frac{\lambda}{RT}\right) \tag{3}$$

Equation (3) shows that a plot of $\ln(dw/dt)$ against $(\ln w - \lambda/RT)$ gives a straight line of slope n, and by substitution in eqn. (2) we get the value of E.

Alternatively if the conversions x_1, x_2 are used instead of w_1, w_2, eqn. (2) becomes

$$\lambda = \frac{E}{n} = \frac{R\ln\left(\dfrac{1-x_1}{1-x_2}\right)}{1/T_1 - 1/T_2} \tag{4}$$

The conversion, x, being defined by $x = 1 - w/w_0$, where w_0 = initial weight of the sample.

It is worth noting that the merit of this method is that it makes use of the DTG reading which is directly proportional to the depth of the DTG trace at any particular point.

EXPERIMENTAL RESULTS AND DISCUSSION

Equilibrium decomposition of $MnCO_3$ (in air)

The manganese carbonate used was supplied by May and Baker Ltd., and was stated to be of 99.95% purity. By screen analysis, the average particle size was found to be 0.071 mm. Microscopic examination of the powder showed it to consist of spherical particles.

Figure 2 shows the equilibrium weight loss against temperature as obtained by heating the powder at different temperatures to constant weight in a thermobalance.

The slight weight loss starting at about 100°C corresponds to evolution of physical water, then at 185°C a sharp drop in weight takes place. By calculating the weight loss this was found to correspond to the reaction

$$MnCO_3 + \tfrac{1}{2}O_2 = MnO_2 + CO_2$$

Then from 190 to 420°C, progressive weight loss took place due to the non-stoichiometry of MnO_2 [4].

Kinetics of the reaction

Isothermal decomposition

Figure 3 shows the conversion, x, as function of time (days) for decomposition and oxidation of $MnCO_3$ at 190°C. Full reaction took place after about 30 days.

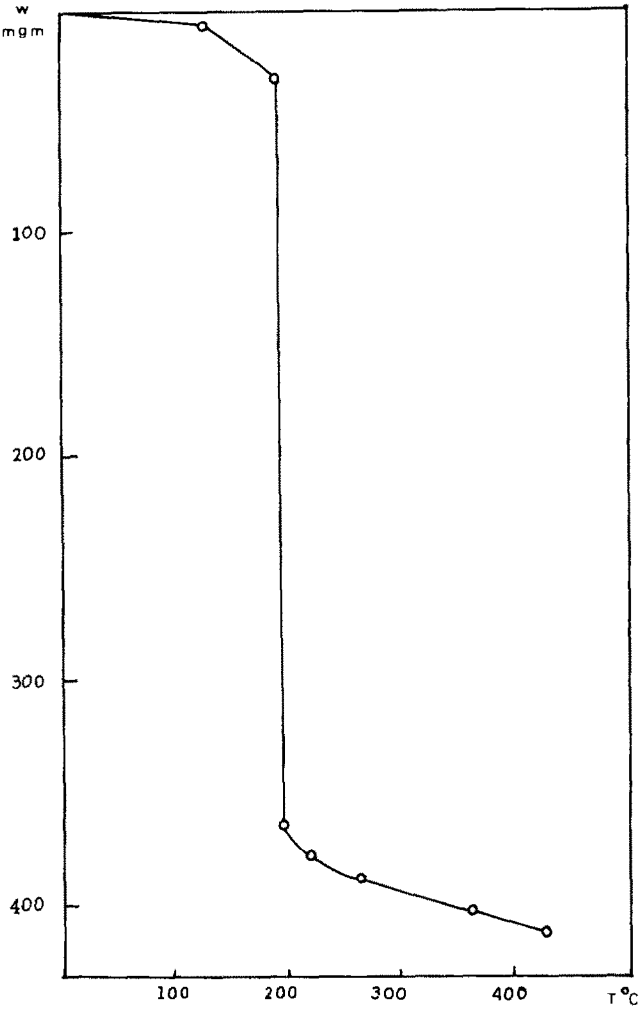

Fig. 2. Equilibrium weight loss for $MnCO_3$.

Figure 4 shows the plot obtained by assuming that this reaction is phase boundary motion controlled. According to Levenspiel [5] when the chemical reaction transformation proceeds leaving an unreacted core, and this chemical reaction controls the process, then

$$\frac{t}{T} = 1 - (1 - x)^{1/3}$$

where t = time, T = time required for complete reaction of particle, x = fractional conversion.

As seen from Fig. 4 the plot is linear, except for the early stage of conversion; the slope of the plot of $1 - (1 - x)^{1/3}$ against time should give $1/T$. From the figure, it was found that $1/T = 0.0348$ day^{-1} or $T = 28.7$

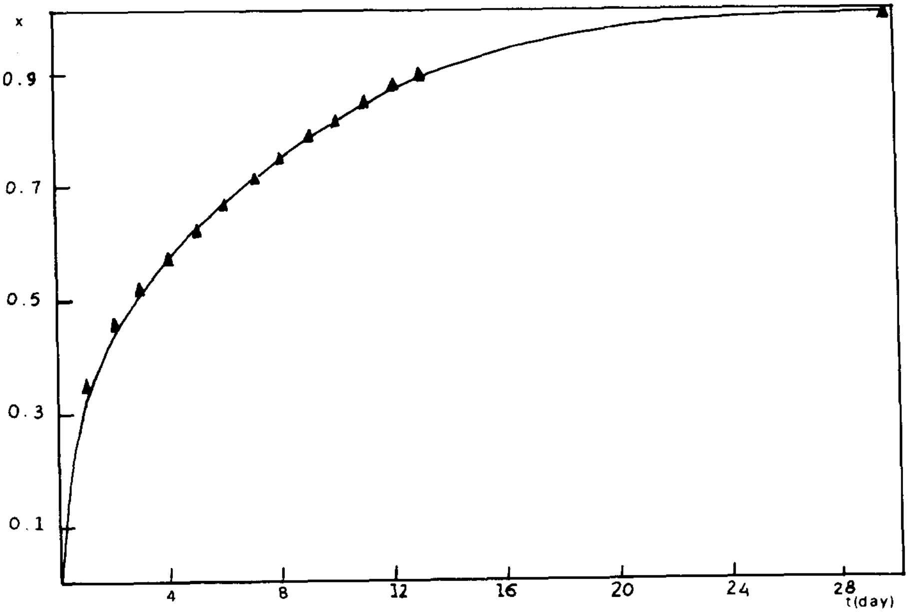

Fig. 3. Conversion–time dependence for the decomposition of $MnCO_3$.

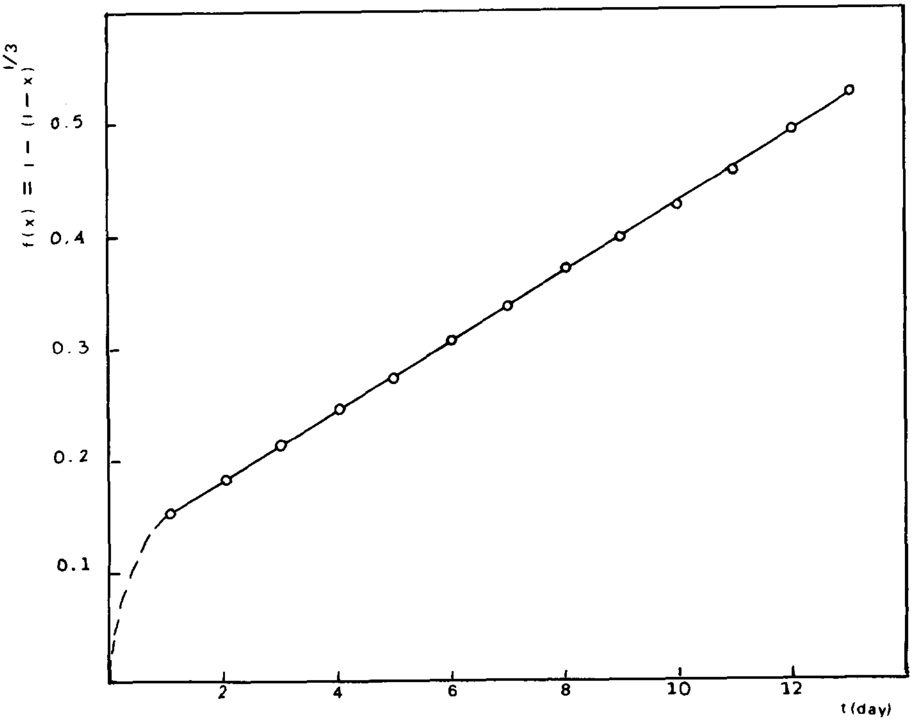

Fig. 4. f(x)–time relationship assuming phase boundary motion controlling the decomposition of $MnCO_3$.

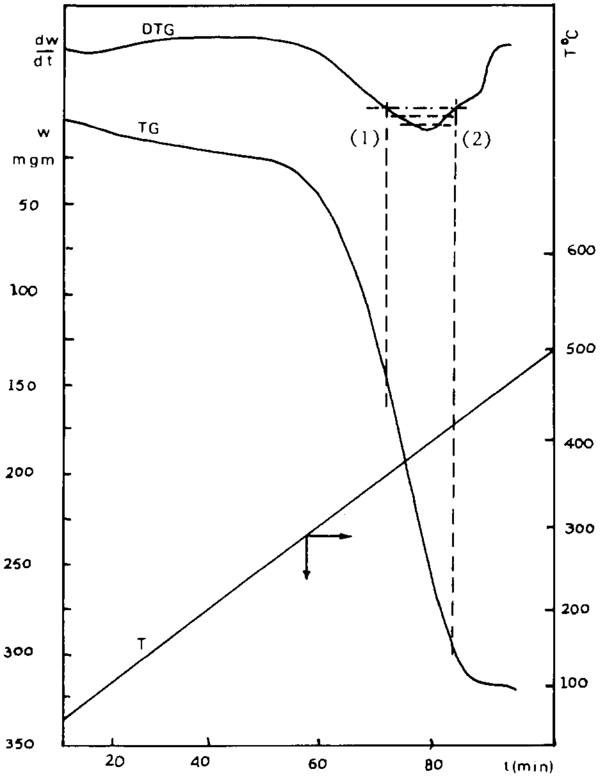

Fig. 5. Derivatogram for $MnCO_3$ with a heating rate of 5°C min^{-1}.

days. This is in excellent agreement with the value $T = 30$ days obtained experimentally.

It was concluded that this reaction is controlled by the motion of the phase boundary between the unreacted core and the ash layer formed. Because of the spherical nature of particles, this motion occurs in three dimensions.

Non-isothermal results

Since this reaction is phase boundary motion controlled, then $t/T = 1 - (1 - x)^{1/3}$. And by differentiation with respect to x we obtain

$$\frac{dx}{dt} = \frac{3}{T}(1 - x)^{2/3} = k(1 - x)^{2/3}$$

Hence, the method proposed for the treatment of thermal curves can be used since $f(x)$ takes the form $(1 - x)^n$.

Figure 5 shows the derivatogram obtained at a heating rate of 5°C min^{-1} in an alumina crucible. The DTG trace gives dw/dt against time, while the TG trace gives w against time. Peak (1) corresponds to the decomposition

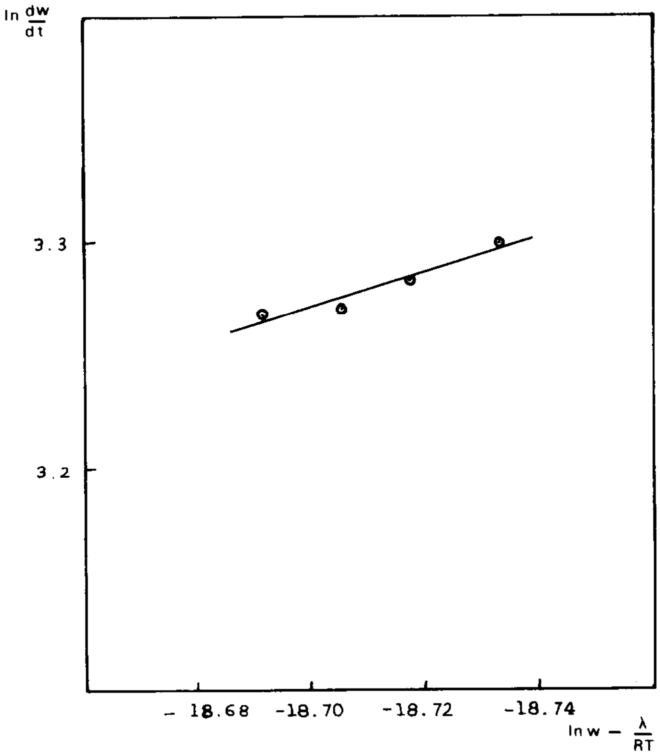

Fig. 6. Plot for calculating n and E for the reaction.

reaction while peak (2) is due to the progressive weight loss of non-stoichiometric MnO_2.

Several pairs of equal values of $\mathrm{d}w/\mathrm{d}t = Ae^{-RT}(1-x)^n$ were equalized to give the value of $\lambda = E/n$, according to eqn. (4).

The value of λ obtained for each pair was nearly constant and the average value obtained for λ was 32230 cal mol^{-1} or 134890 J mol^{-1}.

Figure 6 shows a plot of $\ln \mathrm{d}w/\mathrm{d}t$ vs. $\ln w - \lambda/RT$. The slope of the straight line is $n = 0.76$. The expected value of n should have been 0.67. However, as pointed out by Hilling [6] no credit should be given to values of n obtained from the TG curve. Rather, the obtained value of n means that the empirical equation that describes this reaction at a heating rate R (°C min^{-1}) in air is

$$\frac{\mathrm{d}x}{\mathrm{d}t} = Ae^{-E/RT}(1-x)^{0.76}$$

As $\lambda = E/n$, we get $E = 102030$ J mol^{-1} or 22.4 kcal mol^{-1} which is in excellent agreement with the value of Razouk et al. [7] who obtained $E = 22.5$ kcal mol^{-1}.

CONCLUSIONS

$MnCO_3$ dissociates in air under equilibrium conditions at 185°C with simultaneous oxidation giving off MnO_2. The reaction was found to be controlled by chemical reaction at the phase boundary with $E \approx 102$ kJ^{-1}.

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