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MATHEMATICAL MODELS OF THE KINETICS OF DYNAMIC THERMOGRAVIMETRY

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ABSTRACT

Mathematical models of the kinetics of nucleation growth and interfacial reaction which are suitable for dynamic thermogravimetry are established by investigating the processes of the thermal decomposition of lead carbonate. The models are represented by

$$\ln\left[\left(\frac{\alpha}{1-\alpha}\right)/T^2\right] = \ln\left\{\frac{4\pi r_0^3 AR}{3BE}\left(1-\frac{2RT}{E}\right)\right\} - \frac{E}{RT}$$

and

$$\ln\left\{\left[1-(1-\alpha)^{1/3}\right]/T\right\} = \ln\left\{\frac{AMe^b}{r_0\rho B(E+aR)}\left(1-\frac{RT}{E+aR}\right)\right\} - \frac{E+aT}{RT}$$

The thermal decomposition reactions of lead carbonate are given as:

$$2PbCO_3(s) = PbCO_3\cdot PbO(s) + CO_2 \qquad \text{(I)}$$

$$3(PbCO_3\cdot PbO)(s) = 2(PbCO_3\cdot 2PbO)(s) + CO_2 \qquad \text{(II)}$$

$$PbCO_3\cdot 2PbO(s) = 3PbO(s) + CO_2 \qquad \text{(III)}$$

The activation energies of these reactions obtained from the models are 178.60, 208.20 and 232.79 kJ mol^{-1}, respectively. The experimental results show that the mathematical models of non-isothermal kinetics are valid, reliable, and practical.

INTRODUCTION

A single thermogravimetric (TG) curve is equivalent to a very large number of isothermal curves of residual-weight fraction versus time. Therefore it is particularly important to have an efficient method for analysing this kind of curve. In studying the kinetics of the thermal decomposition of a solid, the method of non-isothermal kinetics proposed by Doyle [1] is worthy of note. Recently, the present author tried to establish mathematical models of the kinetics of dynamic thermogravimetry by investigating the thermal decomposition processes of lead carbonate.

MATHEMATICAL MODELS

A shrinking unreacted core model, shown in Fig. 1, was adopted. The following assumptions were made: that the grain fineness of the solid approaches uniformity; that the thermal decomposition processes of the solid are first-order irreversible; and that the overall rate of solid decomposition is equal to n times the decomposition of one spherical grain.

Nucleation growth model

According to the Erofeev equation

$$\alpha = 1 - \exp(-kt^n) \tag{1}$$

Taking into account the change in the crystal core numbers and the overlap among crystals, the rate of nucleation growth is given by [2]

$$\frac{d\alpha}{dt} = \tfrac{4}{3}\pi k_1 n' k_g^3 t^3 (1-\alpha) \tag{2}$$

where α, t and π have the usual meanings, k_1 and k_g are the rate constant of nucleation ($\text{cm}^{-3}\ \text{s}^{-1}$) and the rate constant of radial nucleation growth (cm s^{-1}), respectively, and n' is the number of latent centres of nucleation. Because $\alpha = 1 - r^3/r_0^3$, $k_g t = r$ and $k_1 n' = k$, eqn. (2) becomes:

$$-\frac{3}{r^4}\frac{dr}{dt} = \tfrac{4}{3}\pi k \tag{3}$$

where r_0 and r correspond to the radii (cm) of the solid grains at the temperatures (K) T_0 and T, respectively. By putting the linear heating rate $B = dT/dt$ (K s^{-1}) and the Arrhenius rate constant $k = A\exp(-E/RT)$ into eqn. (3) and integrating over the intervals $[r_0, r]$ and $[T_0, T]$, where T_0 is taken as zero for practical purposes [1], we obtain

$$\frac{\alpha}{1-\alpha} = \frac{4\pi r_0^3 AE}{3BR}p(x) \tag{4}$$

where A, E, and R have the usual meanings and the exponential integral is $p(x) = (e^x/x^2)(1 + 2!/x + 3!/x^2 + \dots)$ with $x = -E/RT$. Thus the

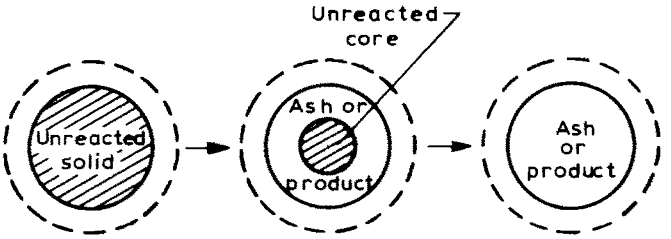

Fig. 1. A gas–solid reaction proceeding with the formation of a shrinking unreacted core.

mathematical model of the kinetics of nucleation growth is found by using two-terms of $p(x)$ and then taking the natural logarithm of eqn. (4)

$$\ln\left[\left(\frac{\alpha}{1-\alpha}\right)/T^2\right]=\ln\left\{\frac{4\pi r_0^3AR}{3BE}\left(1-\frac{2RT}{E}\right)\right\}-\frac{E}{RT} \tag{5}$$

Interfacial reaction model

The rate equation of an interfacial reaction can be written

$$-\frac{\mathrm{d}r}{\mathrm{d}t}=\frac{kMC}{\rho} \tag{6}$$

where M and ρ are the molecular weight and the density of the solid reactant, respectively, and C is the concentration of a gas product decomposed at the reaction interface. By putting $C=P/RT$, with $P=\exp(-a/T+b)$, and $B=\mathrm{d}T/\mathrm{d}t$ into eqn. (6) and integrating

$$\int_{r_0}^{r}-\mathrm{d}r=\frac{AMe^b}{\rho BR}\int_{T_0}^{T}\frac{\exp[-(E+aR)/RT]}{T}\,\mathrm{d}T \tag{7}$$

where a and b are constants. The integral of the right-hand side of eqn. (7) can be written as

$$\int_{T_0}^{T}\frac{\exp[-(E+aR)/RT]}{T}\,\mathrm{d}T=\int_{-\infty}^{x}-\frac{\exp x}{x}\,\mathrm{d}x \tag{8}$$

where $x=-(E+aR)/RT$ and $T_0=0$ K. On the basis of the exponential integral $p(x)$

$$p(x)=-\frac{\exp x}{x}+\int_{-\infty}^{x}\frac{\exp x}{x}\,\mathrm{d}x \tag{9}$$

By rearranging the terms in eqn. (9) we have

$$\begin{aligned}-\int_{-\infty}^{x}\frac{\exp x}{x}\,\mathrm{d}x&=-\frac{\exp x}{x}-p(x)\\&=-\frac{\exp x}{x}\left(1+\frac{1!}{x}+\frac{2!}{x^2}+\dots\right)\end{aligned} \tag{10}$$

where a series of the right-hand side of eqn. (10) is represented by $p'(x)$ which is termed a negative exponential integral. Therefore, on integration, eqn. (7) becomes

$$1-(1-\alpha)^{1/3}=\frac{AMe^b}{r_0\rho BR}p'(x) \tag{11}$$

Thus the mathematical model of the kinetics of the interfacial reaction is found by using two-terms of $p'(x)$ and then taking the natural logarithm of eqn. (11)

$$\ln\left\{\left[1-(1-\alpha)^{1/3}\right]/T\right\}=\ln\left\{\frac{AMe^{b}}{r_0\rho B(E+aR)}\left(1-\frac{RT}{E+aR}\right)\right\}-\frac{E+aR}{RT} \tag{12}$$

Coats–Redfern model [3]

The Coats–Redfern model is expressed as

$$\ln\{[-\ln(1-\alpha)]/T^{2}\}=\ln\left\{\frac{AR}{BE}\left(1-\frac{RT}{E}\right)\right\}-\frac{E}{RT} \tag{13}$$

EXPERIMENTAL RESULTS

The sample used in the experiment was a chemically pure powder of lead carbonate ($\geqslant$ 99.66% wt.). The average diameter of the grains was 5.6×10^{-4} cm. The TG and differential thermal analysis (DTA) curves were obtained by using a Beijing LCT-1 thermobalance which has a sensitivity of weight of ±0.1 mg and an accuracy of temperature of ±1°C. The following experimental conditions were used: the TG–DTA sample holder was a cylindrical alumina crucible of 0.15 ml volume; sample weight of 100 mg; linear heating

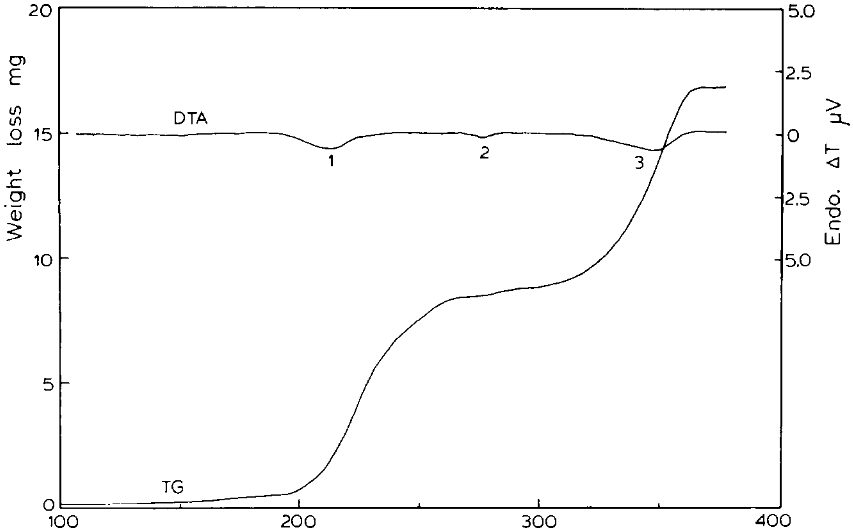

Fig. 2. The TG and DTA curves of the thermal decomposition of lead carbonate in air.

TABLE 1

The values of α and the corresponding to temperatures (T)

Reaction (I)		Reaction (II)		Reaction (III)	
T (K)	α	T (K)	α	T (K)	α
473	0.0842	573	0.1017	618	0.2162
483	0.1930	583	0.1797	620	0.3102
493	0.3860	593	0.3390	623	0.4605
503	0.6433	598	0.4576	628	0.6955
513	0.8012	603	0.6271	633	0.8741
523	0.8865	606	0.7458	638	0.9774

rate of 1 K min^{-1}; the reference material was inert alumina; air atmosphere; recording-paper rate of 1 mm min^{-1}.

The TG and DTA curves of the thermal decomposition of lead carbonate are shown in Fig. 2 where the endothermal peaks 1, 2, and 3 on the DTA curve are represented by the following reactions, respectively [4]

(I) $2PbCO_3(s) = PbCO_3 \cdot PbO(s) + CO_2$ 200–260 °C

(II) $3(PbCO_3 \cdot PbO)(s) = 2(PbCO_3 \cdot 2PbO)(s) + CO_2$ 270–336 °C

(III) $PbCO_3 \cdot 2PbO(s) = 3PbO(s) = CO_2$ 336–370 °C

The relationships between the equilibrium pressures (p) of the above-mentioned reactions and temperature are [5]

(I) $\ln p = -12\,335/T + 22.98$

(II) $\ln p = -10\,750/T + 16.24$

(III) $\ln p = -14\,258/T + 20.06$

The values of α and the corresponding temperatures are listed in Table 1.

DISCUSSION

The thermal decomposition processes of inorganic carbonates, such as lead carbonate which is an essential component of lead oxide ore, are rather complicated [4]. Some studies have been made on the kinetics of the thermal decomposition of lead carbonate. Bruzs [6], Kadlets and Dubinin [7] and Samal [8] have used isothermal methods to study the kinetics of lead carbonate decomposition directly into lead oxide. The activation energies obtained by these authors were 288.9, 173.8, and 168.3 kJ mol^{-1}, respectively. Zivkovic [9] considered that the thermal decomposition of lead carbonate comprises two steps which are controlled by the interfacial reaction: the processes are

$3PbCO_3 = 2PbO \cdot PbCO_3 + 2CO_2$

$2PbO \cdot PbCO_3 = 3PbO + CO_2$

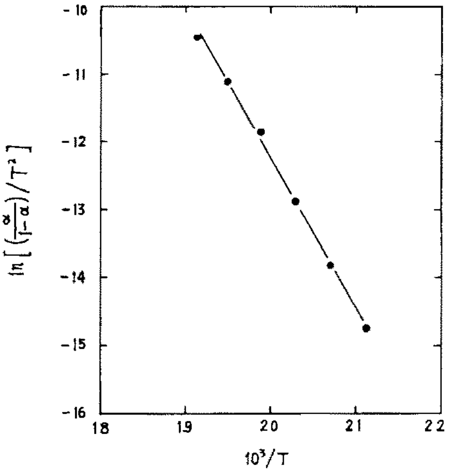

Fig. 3. The plot of ln{[$\alpha/(1-\alpha)$]/T}, versus $1/T$ for reaction (I).

The activation energies of the above-mentioned reactions were found to be 118.2 and 235.2 kJ mol^{-1}, respectively.

The data in Table 1 are linearly described by eqns. (5), (12) and (13). It has been found that the data of reactions (I), (II), and (III) are described correctly by eqns. (5), (13) and (12), respectively. The results of this analysis are shown in Figs. 3–5. The related coefficients of the lines in Figs. 3–5 are 0.9986, 0.9878 and 0.9872, respectively. The pre-exponential factors and the activation energies calculated using the least-squares method are given in

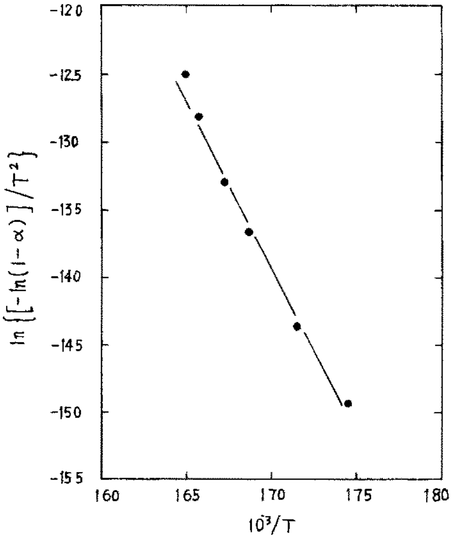

Fig. 4. The plot of ln{[$-\ln(1-\alpha)$]/T^2} versus $1/T$ for reaction (II).

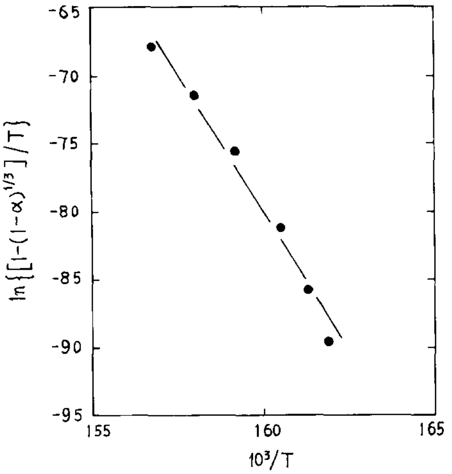

Fig. 5. The plot of $\ln\{[1-(1-\alpha)^{1/3}]/T\}$ versus $1/T$ for reaction (III).

TABLE 2

Values of *A* and *E* for reactions (I)–(III)

Reaction	*A*	*E* (kJ mol^{-1})
(I)	$8.79 \times 10^{25}\ \mathrm{s}^{-1}\,\mathrm{cm}^{-3}$	178.600
(II)	$1.22 \times 10^{15}\ \mathrm{s}^{-1}$	208.200
(III)	$1.26 \times 10^{13}\ \mathrm{cm\ s}^{-1}$	232.790

Table 2. It is seen from Table 2 that the activation energies are in good agreement with those reported in the literature [7–9].

CONCLUSION

The results show that the mathematical models of the kinetics of the thermal decomposition of a solid are in good agreement with the thermogravimetric data. The processes of the thermal decomposition of lead carbonate in air are controlled by nucleation growth, stochastic nucleation, and the interfacial reaction, respectively. The Arrhenius rate equations of the reactions are

$$\begin{array}{lll} \text{reaction (I)} & k = 8.79 \times 10^{25} \exp(-178600/RT) & (\mathrm{s}^{-1}\,\mathrm{cm}^{-3}) \\ \text{reaction (II)} & k = 1.22 \times 10^{15} \exp(-208200/RT) & (\mathrm{s}^{-1}) \\ \text{reaction (III)} & k = 1.26 \times 10^{13} \exp(-232790/RT) & (\mathrm{cm\ s}^{-1}) \end{array}$$

REFERENCES

1 C.D. Doyle, J. Appl. Polym. Sci., 15 (1961) 286.
2 H. Qiyong, Kinetics of Metallurgical Processes, Metall. Industrial Press, Beijing, 1983, p. 53 (in Chinese).
3 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
4 D. Tao, J. Kunming Inst. Technol., 3 (1986) 50 (in Chinese).
5 E.A. Peretti, J. Am. Ceram. Soc., 5 (1957) 171.
6 M. Bruzs, J. Phys. Chem., 30 (1926) 680.
7 O. Kadlets and M.M. Dubinin, Isv. Akad. Nauk. SSSR., 9 (1958) 1031.
8 G.I. Samal, Heterogeneous Chemical Reactions, Moscow, 1961, p. 62.
9 Z.C. Zivkovic, J. Therm. Anal., 16 (1979) 3.