

Improve the Applicability of Rate Equation Based on the Model of Diffusion under Non-isothermal Conditions

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Abstract. Rate equation of non-isothermal kinetics of solid decomposition involving the factors of the pressure of gaseous product, the equilibrium pressure, temperature and structure parameters of solid is deduced according to the model of the diffusion of gaseous product. A validity function in the rate equation of non-isothermal kinetics is defined which represents the influence of these factors on the diffusion rate. The effect of the validity function on the diffusion rate are studied, based on the results of thermal analysis of decomposition of calcium carbonate at different heating rates. It is shown that it is possible to improve the validity of the rate equation of non-isothermal kinetics if the effect is taken into account.

Introduction

Kinetic analysis of solid state decompositions is usually based on a single step kinetic equation [1]

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

where A is the pre-exponential factor, E is the activation energy, T is the temperature, R is the gas constant, α is the extent of conversion, t is the time and $f(\alpha)$ is a function that represents the reaction model, which springs from the hypothetical ideal model, involving interface reactions, diffusion of gaseous product and nuclei growth of solid product [2,3].

Under non-isothermal conditions in which a sample is heated at a constant rate, $\beta = dT/dt$ [4], the explicit temporal dependence in Eq. (1) is eliminated through the trivial transformation

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (2)$$

where β is the heating rate.

Because some workers reported reasonable inconsistent[5] between the Arrhenius parameters estimated from isothermal and non-isothermal measurements. It is evidence that the rate equation of non-isothermal kinetics was invalid. In order to avoid this inconsistency of Arrhenius parameters derived from isothermal and non-isothermal experiments. The rate equation of non-isothermal

kinetics has been corrected by some authors as following way: i) the $f(\alpha)$ has been replaced by an accommodation function or an experience function [6]. ii) the $k(T)$ has been replaced by the others rate constant [7]. iii) integrating the pressure correct term of gaseous product into the rate equation of non-isothermal kinetics[8].

It is noteworthy that analysis of non-isothermal kinetics allows for the global measurement of the reaction process over a wide range of temperature. The rate of diffusion of the gaseous product through the porous solid product layer is influenced by the pore size and irregularity. The values of porosity and tortuosity may be vary with extent of reaction because the reactant or product of solid be subject to sintering or other chemical and physical processes in the decomposition process. Therefore, the influences of the pressure and structure parameters of solid on the rate equation of diffusion may be not neglected in reaction process.

In this paper, the rate equation of non-isothermal kinetics which include the pressure of gaseous product, the temperature, the equilibrium pressure and structure parameters of solid have been developed, based on to the models of diffusion of gaseous product. The influences of these factors on the rate equation of non-isothermal kinetics have been discussed on the basis of the data for the thermal decomposition of calcium carbonate at different heating rates.

Experimental

As experimental examples we have chosen thermal decomposition of chemical reagent of calcium carbonate, average particle-size of sample is $10.27 \mu\text{m}$, and the mass of sample is $20 \pm 0.5 \text{mg}$. The thermogravimetric analysis experiments were carried out using a thermal Analyzer, LABSYS evo, which is made in Setaram of France. The temperature range is from ambient to 1600°C , with heating rate from 0.1 to 50 K/min. The isothermal temperature precision is 0.01°C . The thermocouple is positioned immediately under the sample. The thermal history is determined by the analyzer controller after a standard calibration procedure in the proper conditions. The weighing capacity is 50 mg with a sensitivity of $0.1 \mu\text{g}$. Sample was placed in corundum crucible and heated in atmosphere air. For experiments carried out under non-isothermal conditions, the instrument was programmed to heat the sample from room temperature to 1200°C at a constant heating rate. Four heating rate programs are studied: 10, 20, 30 and 50 K/min.

Theory

The rate equation of non-isothermal conditions for diffusion. For the decomposition reaction (1), it is simpler than the reaction which included the gaseous reactant. Therefore, the rate equations of different steps is deduced, based on the model of gas-solid reaction [9]. The rate equation for diffusion-limited reaction in three dimensions is expressed by the following

$$\frac{d\alpha}{dt} = \frac{2D_e}{r_0^2 \rho R} \frac{(p_B^* - p_B^0)}{T} \frac{3}{2[(1-\alpha)^{-1/3} - 1]} \quad (3)$$

where D_e is the effective diffusion coefficient.

The dependence of D_e on structure parameters of solid is expressed by the following form [10]

$$D_e = \varepsilon \xi D_B \quad (4)$$

where D_B is the diffusion coefficient of the gaseous product, ε is the porosity and ξ is the tortuosity.

The diffusion coefficient D_B in solids is strongly dependent on temperature and follows the Arrhenius equation :

$$D_B = D_{B_0} \exp\left(-\frac{E'_B}{RT}\right) \quad (5)$$

where E'_B is the diffusion activation energy and D_{B_0} is the diffusion coefficient of gaseous product in standard state.

Substituting Eqs. (4) and (5) into Eq. (3), we obtain

$$\frac{d\alpha}{dt} = \frac{2D_{B_0}}{r_0^2 \rho R} \varepsilon \xi \frac{(p_B^* - p_B^0)}{T} \exp\left(-\frac{E'_B}{RT}\right) \frac{3}{2[(1-\alpha)^{-1/3} - 1]} \quad (6)$$

Introducing the heating rate β into Eq. (6), the rate equation of non-isothermal kinetics of a diffusion-limited reaction can be given as follows

$$\begin{aligned} \frac{d\alpha}{dT} &= \frac{A_B}{\beta} f_B(p_B^0, T, p_B^*, \varepsilon \xi) \exp\left(-\frac{E'_B}{RT}\right) f_B(\alpha) \\ &= \frac{2D_{B_0}}{r_0^2 \rho R} \varepsilon \xi \frac{(p_B^* - p_B^0)}{T} \exp\left(-\frac{E'_B}{RT}\right) \frac{3}{2[(1-\alpha)^{-1/3} - 1]} \end{aligned} \quad (7)$$

where A_B is the pre-exponential factor of diffusion, $A_B = 2D_{B_0} / \beta r_0^2 \rho R$, $f_B(\alpha)$ is a function that represents the reaction model of an diffusion-limited reaction, $f_B(\alpha) = 3/2[(1-\alpha)^{-1/3} - 1]$ and $f_B(p_B^0, T, p_B^*, \varepsilon \xi)$ is a function that represents the influence of the reactant or product of solid subjected to sintering or else chemical and physical processes on the rate of diffusion, $f_B(p_B^0, T, p_B^*, \varepsilon \xi) = \varepsilon \xi (p_B^* - p_B^0) / T$.

The validity of rate equation of non-isothermal. Eq. (7) can be described by an equation of the general form

$$\left. \frac{d\alpha}{dT} \right|_m = \frac{A}{\beta} f_B(p_B^0, T, p_B^*, \varepsilon \xi) \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (8)$$

where subscript m indicates the rate equation of non-isothermal kinetics at different rate-determining steps, $f_B(p_B^0, T, p_B^*, \varepsilon \xi)$ is a function that represents the influence of different factors ($p_B^0, T, p_B^*, \varepsilon \xi$) on the rate equation of non-isothermal kinetics

From Eq. (8), assuming $f_B(p_B^0, T, p_B^*, \varepsilon \xi) = A_1$ we obtain

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

where $A' = AA_1$, A_1 is a constant.

It should be noticed that it is reasonable that the influence of $f_B(p_B^0, T, p_B^*, \varepsilon \xi)$ on the rate equation is neglected under isothermal conditions, because the value of $f_B(p_B^0, T, p_B^*, \varepsilon \xi)$ is a constant. However, kinetic analysis of non-isothermal kinetics allows for the global measurement of the reaction process over a wide range of temperature, and the value of p_B^* changes with increasing temperature. The reactant or product of solid may be subject to sintering or other chemical and physical processes in the decomposition process, and the value of $\varepsilon \xi$ also varies during the course of decomposition reaction with the extent of reaction. Therefore, the $f_B(p_B^0, T, p_B^*, \varepsilon \xi)$ is not a constant for these reasons above mentioned. The validity of rate equation of non-isothermal kinetics has to be effected if the variation of $f_B(p_B^0, T, p_B^*, \varepsilon \xi)$ is neglected.

Comparing Eqs. (8) with (9), we obtain

$$\frac{\left(\frac{d\alpha}{dT}\right)}{\left(\frac{d\alpha}{dT}\right)_m} = \frac{A_1}{f_B(p_B^0, T, p_B^*, \varepsilon\xi)} \quad (10)$$

If the value of $f_B(p_B^0, T, p_B^*, \varepsilon\xi)$ is not equal to A_1 , there is deviation of between $d\alpha/dT$ and $d\alpha/dT|_m$ from Eq. (922), and thus Eq. (2) is inapplicable in non-isothermal kinetics. Therefore, $f_B(p_B^0, T, p_B^*, \varepsilon\xi)$ may be regarded as a validity function of the rate equation from isothermal to non-isothermal kinetics.

Results and Discussions

Fig. 1 shows the derivative weight loss cures (DTG) of the thermal decomposition of calcium carbonate under different heating rates. It is evident that the initial temperature (T_i) of reaction is almost uniform at different heating rates, however, the final temperature (T_f) rises with the increasing of the heating rate.

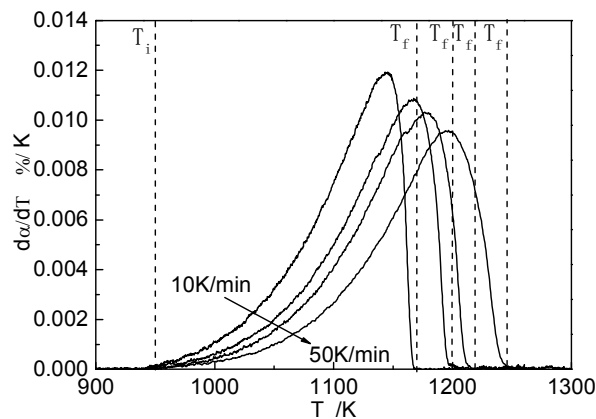


Fig. 1 DTG curves for the thermal decomposition of calcium carbonate at different heating rates.

The validity function of rate equation is obtained from Eq. (7), which is expressed in the following form

$$f_R(p_B^0, T, p_B^*) = (1 - p_B^0/p_B^*)/T \quad (11)$$

For the decomposition reaction of calcium carbonate, the temperature dependence of the equilibrium pressure for the decomposition reaction of calcium carbonate can be expressed by[13]

$$p_B^*/\text{kPa} = 1.87 \times 10^9 \exp\left(-\frac{19697}{T}\right) \quad (12)$$

In order to discuss the influence of the validity function, $f_B(p_B^0, T, p_B^*, \varepsilon\xi)$, on the diffusion rate, we will present two aspects as followed on this discussion. On the one hand, we assume the values of $p_B^0 = 10, 25, 40$ kPa under the structure parameters of solid is a constant ($\varepsilon\xi = 0.5$). By substituting Eq. (12) into Eq. (11), the dependence of f_B on T is illustrated in Fig.2.

As seen from Fig. 2, the value of f_B decreases with increasing of p_B^0 , but it increases with increasing of temperature under the pressure is constant. The variation of maximum value of f_B on completion increases with the increasing of heating rate. The variation of maximum value of f_B is from 0.03 to 0.087 at $\varepsilon\xi = 0.5$ and at $p_B^0 = 10$ kPa, and from 0.02 to 0.07 mol⁻¹ at $\varepsilon\xi = 0.5$ and at $p_B^0 = 40$ kPa with the increasing of heating rate from $10\text{K} \cdot \text{min}^{-1}$ to $50\text{K} \cdot \text{min}^{-1}$. These phenomena evident that the variations of the pressure and temperature have an influence on the diffusion rate.

Therefore, the validity of the rate equation may be improved by integrating the validity function, f_B , into the rate equation of diffusion in non-isothermal kinetics.

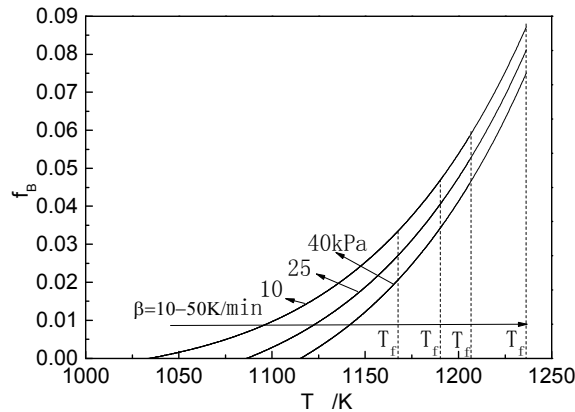


Fig.2 f_B vs T at $\varepsilon\xi = 0.5$ and $p_B^0 = 10, 25, 40$ kPa at different heating rates

On the other hand, assuming that $\varepsilon\xi = 0.1, 0.5, 0.8$ under the pressure is a constant ($p_B^0 = 15$ kPa). By substituting Eq. (12) into Eq. (11), the dependence of f_B on T is illustrated in Fig.3.

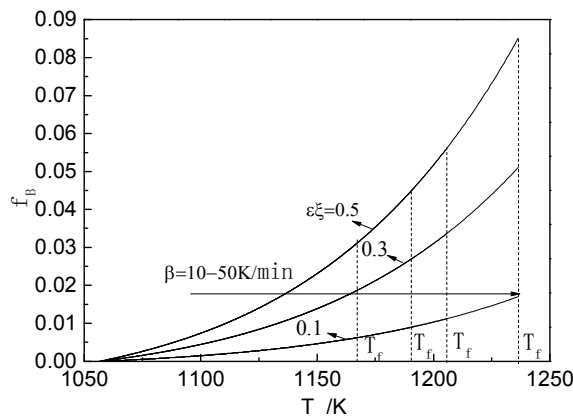


Fig. 3 f_B vs T at $p_B^0 = 15$ kPa and $\varepsilon\xi = 0.1, 0.5, 0.8$ at different heating rates

As seen from Fig. 3, the value of f_B increases with increasing of $\varepsilon\xi$ and temperature under the pressure is constant. The variation of maximum value of f_B on completion increases with the increasing of heating rate. The variation of maximum value of f_B is from 0.06 to 0.01 at $\varepsilon\xi = 0.1$ and at $p_B^0 = 15$ kPa, and from 0.03 to 0.085 mol⁻¹ at $\varepsilon\xi = 0.5$ and at $p_B^0 = 15$ kPa with the increasing of heating rate from 10K·min⁻¹ to 50K·min⁻¹. These phenomena evident that the variations of the structure parameters of solid and temperature have an influence on the diffusion rate. Therefore, the validity of the rate equation may be improved by integrating validity function, f_B , into the rate equation of diffusion in non-isothermal kinetics.

Conclusions

- (1) The rate equations of non-isothermal kinetics of solid decomposition involving the factors of the pressure of gaseous product, the equilibrium pressure, temperature and structure parameter of solid are deduced, based on the models of diffusion of the gaseous product. A validity function which represents the influence of these factors on the rate equation of non-isothermal kinetics is defined.
- (2) The effect of the validity function on the rate of interface reaction and diffusion are studied. It is shown that it is possible to improve the validity of rate equation in non-isothermal kinetics if this effect is taken into account.

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