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IMPROVEMENT OF THE RATE EQUATION BASED ON INTERFACE REACTION AND DIFFUSION FROM ISOTHERMAL TO NON-ISOTHERMAL

ZHONG GUO YANG
College of Engineering， Heilongjiang Bayi Agricultural University, Daqing 163319, Heilongjiang , China

ABSTRACT

Rate equations of non-isothermal kinetics of solid decomposition, which involve the factors of temperature, pressure of gaseous product and structure parameters of solid, are derived from the models of the interface reaction and the diffusion of gaseous product respectively. The definition of the correction term in the rate equations represents the influence of the factors on the reaction rate. The effect of the correction term on rate equations are extrapolated, based on the data of non-isothermal thermal decomposition of calcium carbonate. It is shown that considering the effect of the correction term on rate equations is meaningfully under non-isothermal conditions.

Keywords: *Non-isothermal Kinetics, Correction Term， Temperature, Structure Parameters of Solid, Calcium Carbonate*

1. INTRODUCTION

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

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

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 1 and nuclei growth of solid product [1].

Under non-isothermal conditions in which a sample is heated at a constant rate, $\beta = dT/dt$ [2], the explicit temporal dependence in Eq. (1) is eliminated through the trivial transformation

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

Where β is the heating rate.

This rather trivial transformation bears a great physical meaning. It implicitly assumes that the change in experimental conditions from isothermal to non-isothermal does not affect the reaction kinetics. Since isothermal kinetics had been methodologically well established, they were considered to be the standard that non-isothermal kinetics methods had to match. Therefore, non-isothermal Arrhenius parameters were expected to agree with the isothermal values, but not the other way around. Some workers reported reasonable agreement between the Arrhenius parameters estimated from isothermal and non-isothermal measurements [3-4], but in a number of other cases the values were reported to be inconsistent [5-6]. These disagreements were often considered to provide evidence that the rate equation of non-isothermal kinetics was invalid. The authors of McCallum and Tanner [7] have tried to give a theoretical explanation for inconsistencies in the values of Arrhenius parameters derived from isothermal and non-isothermal experiments. But this theoretical explanation is unsuccessful due to some unreasonable demonstration. 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 [8-10].

In fact, the non-isothermal experiments cover a much wider range of temperatures to measurement of the reaction process. The reaction equilibrium condition is dependent on temperature so that the influence of the deviation of the temperature on the interface reaction may not be neglected in no isothermal kinetics.

The diffusion rate of the gaseous product through the porous solid product layer is influenced by the pore size and irregularity. The influence is presented by effective diffusion coefficient which is modified by porosity and tortuosity. However, the values of porosity and tortuosity may vary with the reaction process because the reactant or product of solid is subjected to sintering or other chemical and physical processes in the decomposition process. Some authors[11]have concluded that the rate constant of decomposition of calcium carbonate include the pressure correction term. The influence of the pressure of gaseous product on the thermal decomposition kinetics of calcium carbonate has been studied [12]. The decomposition pressure representing the driving force of diffusion of the gaseous product through the solid product layer is dependent on temperature. Therefore, the influence of the variation of the pressure of gaseous product, porosity, tortuosity on the diffusion rate may not be neglected under no isothermal conditions.

In this paper, the rate equations, which involve the factors of thermodynamics conditions, the pressure of gaseous product, structure parameters of solid and/or conversion, has been derived from isothermal to non-isothermal based on the models of the interface reaction and the diffusion of gaseous product. The expressions of correction term of different rate-controlling steps involving these factors in non-isothermal kinetics have been established. We have focused our attention on investigating the influence of the variation of correction term on the rate equations of different rate-controlling steps by the data for non-isothermal thermal decomposition of calcium carbonate.

2. THEORY

2.1 Rate Equation Of Non-Isothermal Kinetics

Some authors have proposed that the decomposition reaction takes place on a definite boundary between the undecomposition carbonate and the layer of porous lime formed outside it. This boundary moves towards the center of the sorbent but remains spherical in shape. The rate equations of different rate-controlling steps can be derived, based on the unreached-core shrinking model. If the interface reaction is the rate-controlling step, the rate equation is expressed by the following form [13]

$$\frac{d\alpha}{dt}=\frac{k_R}{r_0\rho R}\frac{(1-p_B^0/K^\Theta)}{T}\exp(-\frac{E_R}{RT})n_R(1-\alpha)^{(n_R-1)/n_R} \qquad (3)$$

where k_R is the pre-exponential factor, E_R is the activation energy of the interface reaction, K^Θ is the equilibrium constant, p_B^0 is the partial pressure of gaseous product, T is the temperature, ρ is the mole density of the solid reactant, r_0 is the radius of the spherical sample and n_R is the number of dimensions in which the interface advances.

Introducing the heating rate β into eq 3, the rate equation of non-isothermal kinetics of an interface-limited reaction can be given as follows

$$\frac{d\alpha}{dT}=\frac{A_R}{\beta}f_R(p_B^0,T,K^\Theta)\exp(-\frac{E_R}{RT})f_R(\alpha) \qquad (4)$$
$$=\frac{k_R}{\beta r_0\rho R}\frac{(1-p_B^0/K^\Theta)}{T}\exp(-\frac{E_R}{RT})n_R(1-\alpha)^{(n_R-1)/n_R}$$

where A_R is the pre-exponential factor of the interface reaction, $A_R=k_R/\beta r_0\rho R$, $f_R(\alpha)$ is a function that represents the reaction model of an interface-limited reaction, $f_R(\alpha)=n_R(1-\alpha)^{(n_R-1)/n_R}$ and $f_R(p_B^0,T,K^\Theta)$ is a function that represents the influence of the thermodynamics conditions on the rate of interface reaction, $f_R(p_B^0,T,K^\Theta)=(1-p_B^0/K^\Theta)/T$.

If the diffusion of gaseous product is the rate-controlling step, the rate equation is expressed by the following form [13]

$$\frac{d\alpha}{dt}=\frac{2D_{B_0}}{r_0^2\rho R}\varepsilon\xi\frac{(K^\Theta-p_B^0)}{T}\exp(-\frac{E_B^{'}}{RT})\frac{3}{2\left[(1-\alpha)^{-1/3}-1\right]} \qquad (5)$$

where D_{B_0} is the diffusion coefficient of gaseous product in standard state, $E_B^{'}$ is the diffusion activation energy, ε is the porosity and ξ is the tortuosity.

Introducing the heating rate β into eq 5, the rate equation of non-isothermal kinetics of a diffusion-limited reaction can be given as follows

$$\frac{d\alpha}{dT}=\frac{A_B}{\beta}f_B(p_B^0,T,K^\Theta,\varepsilon\xi)\exp(-\frac{E_B^{'}}{RT})f_B(\alpha)$$
$$=\frac{2D_{B_0}}{r_0^2\rho R}\varepsilon\xi\frac{(K^\Theta-p_B^0)}{T}\exp(-\frac{E_B^{'}}{RT})\frac{3}{2\left[(1-\alpha)^{-1/3}-1\right]} \qquad (6)$$

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, $f_B(\alpha)=3/2\left[(1-\alpha)^{-1/3}-1\right]$ and $f_B(p_B^0,T,K^\Theta,\varepsilon\xi)$ 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 diffusion rate , $f_B(p_B^0,T,K^\Theta,\varepsilon\xi)=\varepsilon\xi(K^\Theta-p_B^0)/T$.

2.2 The Correction Term Of Rate Equation Of Non-Isothermal

Esq. 4 and 6 can be described by an equation of the general form

$$\left.\frac{d\alpha}{dT}\right|_s=\frac{A}{\beta}f(l_1,l_2,\ldots)\exp(-\frac{E}{RT})f(\alpha) \qquad (7)$$

Where subscript s indicates the rate equation of non-isothermal kinetics which developed according to different rate-controlling steps, $f(l_1,l_2,\ldots)$ is a function that represents the influence of different factors ($f(l_1,l_2,\ldots)$) on the rate equation of non-isothermal kinetics and $l_1,l_2,\cdots$ represents $p_B^0,T,\ldots$ respectively.

As seen from eq 7, if the value of $f(l_1,l_2,\ldots)$ is a constant, the eq 2 is meaningfully applicable to describe the kinetics behavior at different rate-controlling steps. Actually, 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 K^Θ 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 $\varepsilon\zeta$ also varies during the course of decomposition reaction with the extent of reaction. One can deduce from these reasons that the $f(l_1,l_2,\ldots)$ is not a constant during the cause of the reaction. Therefore, the $f(l_1,l_2,\ldots)$ may be regarded as a correction term of the rate equation from isothermal to non-isothermal kinetics.

The correction term for any single-step reaction can be extrapolated with the rate equation (7). For example, the correction term ($f_R(l_1,l_2,\cdots)$) of rate equation of interface reaction is obtained from Eq. (4), which is expressed in the following form

$$f_R(l_1,l_2,\ldots)=(1-p_B^0\big/p_B^*)\big/T \qquad (8)$$

The correction term ($f_B(l_1,l_2,\ldots)$) of rate equation of diffusion of gaseous product is obtained from Eq. (6), which is expressed in the following form

$$f_B(l_1,l_2,\ldots)=\varepsilon\xi\,(p_B^*-p_B^0)\big/T \qquad (9)$$

3. EXPERIMENTAL SECTION

As experimental examples we have chosen thermal decomposition of chemical reagent of calcium carbonate, average particle-size of sample is 10.27 μm, and the mass of sample is 20±0.5mg. The thermo gravimetric analysis experiments were carried out using a thermal Analyzer, LABSYS evo, which is made in Seta ram of France. The temperature range is from ambient to 1600℃, with heating rate from 0.1 to 50 K/min. The isothermal temperature precision is 0.01℃. The thermocouple is positioned immediately under the sample. The thermal history is determined by the analyzer controller after a standard calibration procedure under the proper conditions. The weighing capacity is 50 mg with a sensitivity of 0.1 μg . 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℃ at a constant heating rate. Four heating rate programs are studied: 10, 20, 30 and 50 K/min.

4. RESULT AND DISCUSSION

4.1 The Effect Of $f_R(l_1,l_2,\ldots)$ On The Interface Reaction Rate

For the decomposition reaction of calcium carbonate, the relationship between the equilibrium constant and the equilibrium of pressure of the gaseous product is expressed by the following form

$$\Delta G^0=-RT\ln K^\Theta=-RT\ln p_B^* \qquad (10)$$

Where ΔG^0 is the standard Gibbs free energy for the reaction and p_B^* is the equilibrium of pressure of the gaseous product. The temperature dependence of the equilibrium pressure for the decomposition reaction of calcium carbonate can be expressed by

$$p_B^*/\,\mathrm{kPa}=1.87\times10^9\exp(-\frac{19697}{T}) \qquad (11)$$

By substituting eq 11 into eq 8, and the experimental data were processed using this procedure by adopting the value of p_B^0 from reference 13. The dependence of $f_R(l_1,l_2,\ldots)$ on T is illustrated in Fig. 1.

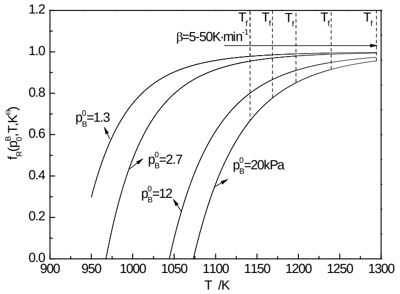

Fig.1 Dependence Of $f_R(l_1,l_2,\ldots)$ On T At Different p_B^0 Determined By The Eq 8 For Different Heating Rates.

As seen from Figure1, we can conclude of the following. (ⅰ)The curves of the $f_R(l_1,l_2,\ldots)$ evidently depends on the temperature and the partial pressure of gaseous product. (ⅱ)At the initial temperature T_i, the value of $f_R(l_1,l_2,\ldots)$ obtained from eq 8 decreases with partial pressure, from about 0.3 to about 0.002 with the increasing of partial pressure from 1.3 to 20 kPa. These behaviors may be indicative of the interface reaction rate may has a low value at beginning of the reaction under at high pressure. (iii) At $\beta = 5\mathrm{K/min}$, the value of $f_R(l_1,l_2,\ldots)$ at the final temperature (T_f) of reaction reduces from about 0.98 to about 0.67 with the partial pressure of gaseous product from 1.3 to 20 kPa. However, At $\beta = 50\mathrm{K/min}$, the value of $f_R(l_1,l_2,\ldots)$ on completion reduces from about 0.99 to about 0.95 with the partial pressure of gaseous product from 1.3 to 20 kPa. These phenomena evident that the variations of the pressure and temperature have an influence on the interface reaction rate. The influence of degree on reaction rate is more and more sharp with increasing of the pressure and the temperature. Therefore, the correction term may be integrated in the rate equation of interface reaction under non-isothermal conditions.

4.2 The Effect Of $f_B(l_1,l_2,\ldots)$ On The Diffusion Rate

In order to discuss the influence of $f_B(l_1,l_2,\ldots)$ on the diffusion rate, we will present two aspects as followed on this discussion. On the one hand, we assumed that the structure parameters of solid are a constant ($\varepsilon\xi = 0.1$). By substituting eq11into eq 9, and adopting the value of partial pressure from reference13. The dependence of $f_B(l_1,l_2,\ldots)$ on T and p_B^0 is illustrated in Figure 2, as determined by the experimental data.

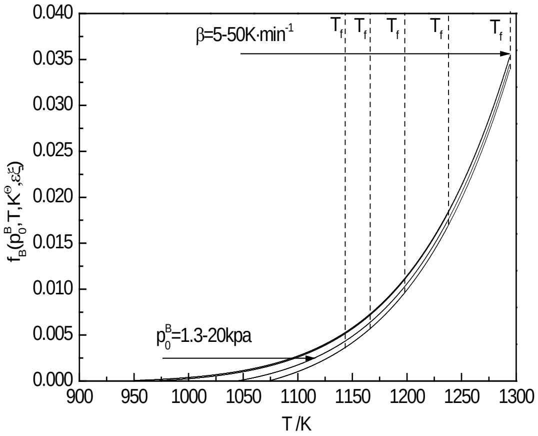

Fig.2 Dependence Of $f_B(l_1,l_2,\ldots)$ On T At Different p_B^0 Determined By The Eq 9 For Different Heating Rates.

As seen from Figure 2, we can be found as the following. (i)The curves of the $f_B(l_1,l_2,\ldots)$ are evidently indicated that $f_B(l_1,l_2,\ldots)$ varies with temperature and partial pressure of gaseous product (ii) At a given value of $p_B^0 = 1.3$ kPa, the value of $f_B(l_1,l_2,\ldots)$ calculated from eq 9 increases with temperature. The value of $f_B(l_1,l_2,\ldots)$ at the final temperature of the reaction increases from 0.0052 to 0.035, because of the T_f increases with the heating rate. But At a given value of $p_B^0 = 20$ kPa, the value of $f_B(l_1,l_2,\ldots)$ at the final temperature of the reaction increases from 0.0035 to 0.03. Consequently, it is clear that these variations have an important influence on the diffusion rate under non-isothermal conditions.

On the other hand, we assumed that the values of $\varepsilon\xi = 0.01, 0.1, 0.5$ under the condition that partial pressure of gaseous product is a constant ($p_B^0 = 2.7$ kPa). By substituting eq 11 into eq 9, and the experimental data shown were introduced using this procedure. The dependence of $f_B(l_1,l_2,\ldots)$ on T is illustrated in Figure 3.

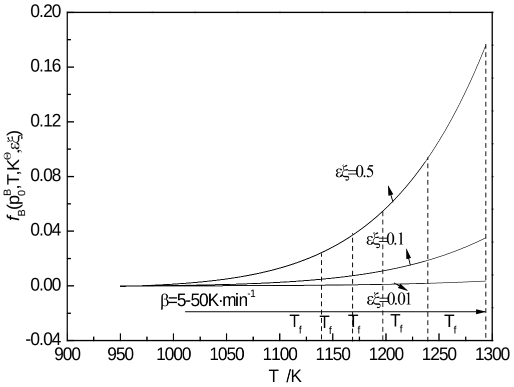

Fig. 3 Dependence Of $f_B(l_1,l_2,\ldots)$ On T At Different $\varepsilon\xi$ Determined By The Eq 9 For Different Heating Rates ($p_B^0 = 2.7$).

From Figure 3, it can be seen that the value of $f_B(l_1,l_2,\ldots)$ varies with temperature and structure parameters of solid. It is demonstrated that the influence of $f_B(l_1,l_2,\ldots)$ on the diffusion rate is not neglected. At $p_B^0 = 2.7$, the value of $f_B(l_1,l_2,\ldots)$ increases with the increasing of $\varepsilon\xi$ and temperature. The value of $f_B(l_1,l_2,\ldots)$ at the final temperature of reaction rises with the heating rate from 5 to $50K/\mathrm{min}$, because of the T_f increases with the heating rate. At $\beta = 5K/\mathrm{min}$, the value of $f_B(l_1,l_2,\ldots)$ at the end of reaction increases from around 0.0005 to around 0.03 with the increasing of $\varepsilon\xi$ from 0.01 to 0.5. However, at $\beta = 50K/\mathrm{min}$, the variation of maximum value of $f_B(l_1,l_2,\ldots)$ at the end of reaction increases from around 0.004 to around 0.2 with the same variation interval of the structure parameters of solid. As a result, the effect of the variation of

$f_B(l_1,l_2,K)$ on the diffusion rate may be not neglected under nonisothermal conditions.

5. CONCLUSIONS

(1) The rate equations of non-isothermal kinetics of solid decomposition involving the factors of the pressure of gaseous product, the equilibrium pressure, and temperature structure parameter of solid are deduced, based on the models of interface reaction and diffusion of the gaseous product. A correction term which represents the influence of these factors on the rate equation of non-isothermal kinetics is defined.

(2) The effect of the correction term on the rate of interface reaction and diffusion are studied. The result is shown that the influence of the correction term on the rate equation may be not neglected from isothermal to no isothermal.

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