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Calculation of Activation Energy in Multiphase Reaction

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Abstract. Most of reactions in the metallurgy are heterogeneous that have a complicated mechanism, for which the kinetic treatment is complex. In general, one has to find the controlling step first, and based on which to derive the corresponding kinetic formula to describe the kinetic behavior. Currently, the most popular method to determine the controlling step is so called the Sharp method, that is, deriving a series of formulae based on different assumed controlling steps in a consecutive heterogeneous reaction, then comparing the experimental data with various kinds of formulae to decide which formula can meet the experiment data well, and from which to select the most suitable controlling step. Nevertheless, because all these formulae used in estimating the controlling step involve some unknown parameters, for instance, the Jander equation, Gingstling-Brounshtein equation, parabolic equation… etc. all involve an unknown parameter "k", that will prevent us from obtaining an accurate activation energy. In this article, we will give a new method based on our series of new formulae concerning the kinetics of multiphase reactions, in which all parameters contained have clear physical meanings, therefore, when they have been used to fit the experimental data, one can obtain a more accurate activation energy and the least relative errors. Some examples have been presented to show the advantages of this new method.

Keywords. Solid state reaction, kinetics, metallurgical kinetics, activation energy.

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1 Introduction

The kinetics of multiphase reaction is an important issue for many fields, such as metallurgy, material sciences, chemical engineering, chemistry, pharmaceutics, biochemistry, geochemistry…etc., among which the treatment required in chemical metallurgy is most complicated and important since many reactions in metallurgy are heterogeneous consecutive reaction with a multicomponent system at an elevated temperature, where experiments are difficult to perform and theoretical treatments are not easy to deal with. Many research results obtained from metallurgical reaction may have general meaning to other fields.

The key issue of studying the kinetics of a reaction involving solid components is to find a model to describe the reaction fraction ξ with reaction time t. In principle, one may need to solve a group of differential equations with initial conditions and boundary conditions to get a result. This method is too complicated and the solution obtained in this way might not be useful for an analytic discussion. Instead, in the history, many models have been proposed based on some assumptions. Currently, the frequent models used for describing these relations are, parabolic method [1], Jander model [2], Ginstling-Brounshtein model [3], reduce time method (Sharp method [4]), model fitting method, model free method [5–7], … and so forth. All these methods have their own characteristics, however, some troubles have been met in applications. First of all, these models are all based on an assumption, that is., the time derivative of the reacted fraction ξ is proportional to the product of function of $f(\xi)$ and the function of temperature, $k(T)$, i.e.

$$\frac{d\xi}{dt} = f(\xi)k(T). \tag{1}$$

On the other words, in the above equation the variable ξ and T can be separated [6–8]. It is an approximation assumption for current models. In some cases, this approximation will cause a big error. Besides, it can be seen that, function $f(\xi)$ and $k(T)$ involve certain constants, the physical meaning of which may not be clear. The function $k(T)$ can be expressed as the Arrhenius equation $k = k_0 \exp(-\frac{\Delta E}{RT})$, the Arrhenius equation in which the k_0 still needs to be evaluated from a practical data system. In sum, because of the above two reasons the current methods might have some calculation errors. Besides, they have other disadvantages that will be discussed in the following sections.

2 The "Real Physical Picture" Model

In order to overcome the drawback of the current traditional models, a new model has been proposed and called as the "Real Physical Picture" (RPP) model here. This model is

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established on a real physical picture associated with an actual reaction mechanism without any assumption made for time derivative of the reacted fraction like that adopted by the current models [9, 11, 12, 19]. Therefore, all parameters in the RPP model have a clear physical meaning that will be easy for reader to judge the reasonableness of the values obtained from a data fitting. For a reaction controlled by the diffusion, the formula should be [9, 10, 12]

$$\xi = 1 - [1 - \frac{1}{R_0}\sqrt{\frac{2D^0 k(\sqrt{P} - \sqrt{P^{\mathrm{eq}}})}{v_m \exp(\frac{\Delta E}{RT})}t}]^3, \quad (2)$$

where D^0 is a constant related to the gas diffusion through a product layer that is independent of temperature, ΔE activation energy, P and P^{eq} are partial pressures of gas in the gas phase and in the interface between reactant and product that is in equilibrium with some solid product respectively. v_{m} a constant related to the reactant and product densities, k a constant of Sieverts' law, R_0 sphere radius, R universal gas constant and T absolute temperature.

If the reaction rate-controlling step is not in the diffusion but in other steps, some different formulae should be expected [11]. It is found that if the rate-controlling step is other than the diffusion (for instance, physisorption, chemisorption, surface penetration, chemical reaction), the rate expressions of them are very similar [11] except for the nucleation controlling-step. Therefore, the expressions of the reaction fraction are also very similar and can be expressed as,

$$\xi = 1 - (1 - \frac{k_1(p - p^{\mathrm{eq}})\exp(-\frac{\Delta\varepsilon_1^f}{RT})}{v_m R_0}t)^3 \quad (3)$$

for physisorption and chemisorption controlled, and formula

$$\xi = 1 - (1 - \frac{k_2(p^{\frac{1}{2}} - p^{\mathrm{eq}\frac{1}{2}})\exp(-\frac{(\Delta H_2^\circ + 2\Delta\varepsilon_2^f)}{2RT})}{v_m R_0}t)^3 \quad (4)$$

for surface penetration, chemical reaction (please check [11] for the meaning of some constants).

The above formulae and treatment are only suitable for the shape of sphere ball. When the sample shape is other than a ball but a cylinder or cuboids, different formulae should be expected as described in our previous papers [12].

3 Comparison of Calculation Error Between RPP Model and other Current Models

In this section, the calculation errors between RPP method and current other methods are compared to see what the difference is. Let us take a parabolic model as an example, when the rate is controlled by the diffusion, the parabolic model is

$$\xi = k\sqrt{t}. \quad (5)$$

Taking logarithm to both sides of the above equation, one has

$$\ln\xi = \ln k + \frac{1}{2}\ln t. \quad (6)$$

The parameter k can be found through the least square regression based on the ξ vs. t data set at a fixed temperature since Eq. (6) should be a straight line. On the other hand, according to the Arrhenius law

$$k = k_0 \exp\left(-\frac{\Delta E}{RT}\right) \quad (7)$$

or

$$\ln k = \ln k_0 - \frac{\Delta E}{RT}. \quad (8)$$

The plot of lnk vs. $1/T$ should be another straight line, after a least square regression, the activation energy ΔE and k_0 can be obtained.

At present let us make a calculation for the whole procedure described above. If originally there is a set of experimental data with 5 groups of data points, each group has 10 points of (ξ, t) associated with five different temperatures. First, in order to find these five "k" values, one has to make regression for five times, then one needs one more regression to extract k_0 and ΔE according to Eq. (8). Totally, six times of regressions are required.

The next, let us take look our model, rearranging Eq. (2) as the following form

$$\xi = 1 - [1 - \sqrt{\frac{\exp(-\frac{\Delta E}{RT})}{\frac{v_m R_0^2}{2D^0 k(\sqrt{P} - \sqrt{P^{\mathrm{eq}}})}}t}]^3. \quad (9)$$

Define

$$B_T = \frac{v_m R_0^2}{2D^0 k(\sqrt{P} - \sqrt{P^{\mathrm{eq}}})}, \quad (10)$$

where B_T is a constant relying on temperature. When the gaseous partial pressures keep constant, B_T should be no change.

Combining Eq. (9) and Eq. (10), the following equation should be obtained

$$\xi = 1 - [1 - \sqrt{\frac{\exp(-\frac{\Delta E}{RT})}{B_T}t}]^3 \quad (11)$$

Now, let us use Eq. (11) to fit our experimental data mentioned above. Eq. (11) is a non-linear equation. There are a lot of simple mathematic programs to deal with the non-linear regression problem, from which one can extract both parameters B_T and ΔE in a simple regression with all 50 data once. More important is that, this method should have a relative smaller calculation error in comparison with the above traditional methods due to only making regression once. Eq. (11) can also be rearranged as the following form

$$\ln[1-(1-\xi)^{\frac{1}{3}}]^2 = -\ln B_T - \frac{\Delta E}{RT} + \ln(t) \qquad (12)$$

to extract B_T and ΔE from a straight line of $\ln[1-(1-\xi)^{\frac{1}{3}}]^2$ vs. $\ln(t)$.

Similarly, Eq. (2) can also be written in the following way

$$\xi = 1 - \left[1 - \sqrt{\frac{(\sqrt{P}-\sqrt{P^{\mathrm{eq}}})}{B_P}t}\right]^3, \qquad (13)$$

where

$$B_P = \frac{R_0^2 v_m \exp(\frac{\Delta E}{RT})}{2D^0 k}. \qquad (14)$$

B_P is also a constant as temperature is fixed. Likewise, the calculation error based on Eq. (13) should have lower errors in comparison with other current methods due to regression once.

4 Examples

MacKenzie et al. [13, 14] have studied the oxidation of β-SiAlON (z=2.45) powder from 1378 to 1578 K, O′-SiAlON ($x = 0.18$) powder from 1353 to 1606 K and x-phase SiAlON powder from 1173 to 1323 K, based on which it is found that the rate-controlling step should be in the oxygen diffusion through the oxide layer, therefore, both parabolic model and our model should be suitable for these data treatments. The activation energies computed by parabolic method are 156.9 kJ/mol, 412.5 kJ/mol, 198.4 kJ/mol respectively for oxidation of β-SiAlON ($z = 2.45$), O′-SiAlON ($x = 0.18$) and x-phase SiAlON, while our method gives the following results: 185.4 kJ/mol, 373.1–655.2 kJ/mol and 279.7 kJ/mol for three corresponding SiAlON powders, in which the O′-SiAlON ($x = 0.18$) has two values due to existing different phases [15]. In order to compare the calculated accuracy for these two methods, the function of the average relative error Δ, is introduced that is defined as

$$\Delta = \frac{1}{N} \cdot \sum_{i=1}^{N} \frac{|(\chi_i)_{\mathrm{mea}} - (\chi_i)_{\mathrm{cal}}|}{|(\chi_i)_{\mathrm{mea}}|} \times 100\%, \qquad (15)$$

where $(\chi_i)_{\mathrm{mea}}$ is the experimental data measured, $(\chi_i)_{\mathrm{cal}}$ is the value calculated from the model and N is the sum of experiment points. According to the experimental data offered by MacKenzie et al. and both parabolic and RPP calculation formulae, the average relative errors calculated by two methods are listed in Table 1, from which it is clearly shown that the average relative error of our method is less than that of the parabolic model.

	Δ (average relative error)	
	Calculated by parabolic model	Calculated our model
β−SiAlON	15.7 %	8.4 %
O′-SiAlON	20.3 %	8.7 %
X-phase	14.4 %	10.6 %

Table 1. Comparison of the average relative error calculated by parabolic model and Chou model.

It was found that the oxidation kinetics of Si_3N_4 is also controlled by the diffusion of oxygen in product layer [16, 17]. Hou et al. [18] measured the oxidation curves of Si_3N_4 powder at 1373 K, 1473 K and 1573 K in air atmosphere (shown in Figure 1). The activation energies computed by parabolic method is 99.2 kJ/mol, while 325.6 kJ/mol by our model which is close to the value 363.0 kJ/mol by Ogbuji et al. [16, 17]. The average relative errors are 11.6 % and 2.6 % for parabolic method and our model, respectively. Comparisons between the calculated curves and those by experiments are given in Figure 1, from which it can be seen that our model works very well.

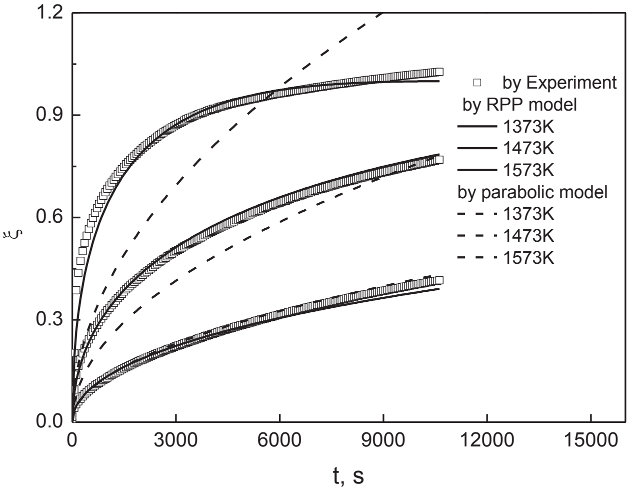

Figure 1. Comparisons between experiment data and model calculated data for oxidation of Si_3N_4.

Another example is related to the hydrogen absorption that is also a typical solid-gas reaction. Kandavel et al. [19–21] had conducted many experiments on the solubility of H_2 gas and diffusion of H interstitials in Zr-based AB_2 alloys $Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.5}Co_{0.5}$, $Ti_{0.1}Zr_{0.9}(Mn_{0.9}V_{0.1})_{1.1}Fe_{0.5}Ni_{0.5}$ and $Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.55}Ni_{0.55}$ prepared by different methods. Based on these experimental data, one can use the Jander model to evaluate the apparent activation of energy since these absorption reaction are controlled by the diffusion of hydrogen through the α phase region under 673 K to 923 K through a set of curve fitting. The calculated results are 26.9 kJ/mol H_2 for $Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.5}Co_{0.5}$, 39.5 kJ/mol H_2 for $Ti_{0.1}Zr_{0.9}(Mn_{0.9}V_{0.1})_{1.1}Fe_{0.5}Ni_{0.5}$ and 47.5 kJ/mol H_2 for $Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.55}Ni_{0.55}$, respectively. For comparison, at present, our model has been used to deal with the same problem. Differing from the Jander model's treatments where the multi-regressions were required, our model only requires regression once. Therefore the average relative error Δ calculated from our method should be smaller than that from Jander model as explained in the previous paragraph (see Table 2). The calculated apparent activation energies from our model are 28.1 kJ/mol H_2 for $Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.5}Co_{0.5}$, 39.03 kJ/mol H_2 for $Ti_{0.1}Zr_{0.9}(Mn_{0.9}V_{0.1})_{1.1}Fe_{0.5}Ni_{0.5}$ and 41.65 kJ/mol H_2 for $Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.55}Ni_{0.55}$, respectively.

Alloy	Δ (average relative error)	
	Calculated by Jander model	Calculated by our model
$Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.5}Co_{0.5}$	24.9 %	3.8 %
$Ti_{0.1}Zr_{0.9}(Mn_{0.9}V_{0.1})1.1Fe_{0.5}Ni_{0.5}$	11.5 %	3.0 %
$Ti_{0.1}Zr_{0.9}Mn_{0.9}V_{0.1}Fe_{0.55}Ni_{0.55}$	9.4 %	4.3 %

Table 2. Comparison of the calculation error from Jander model and Chou model.

5 Discussions

(1) In the data treatment, the regression method has been used to extract the related parameters. In general, one can apply the correlation coefficient to evaluate the curve fitting. The larger the correlation coefficient, the more accurate the value of extracted parameters will be. However, it must be kept in mind that, though the smaller correlation coefficient must correspond to a bad model selected, but the higher correlation coefficient doesn't mean the model used must be a good one. Since any mathematic formula can reach a good fitting, as long as the number of parameters is increased enough in the fitting expression. Therefore, not only the correlation coefficient should be considered, but also the mathematical expression should have a reasonable number of parameters, in which all parameters must have clear physical meaning. Our model is able to meet these requirements.

(2) A small relative average error Δ means that the data fitting is in a good shape, therefore, the correlation coefficient should be large. In the previous section, we have given some examples to show that our method can offer a smaller relative average errors Δ in compared with other traditional methods, and we have further explained why our method works well that should be contributed to require regression for only once in the data treatment, while other methods involve a multi-regression.

(3) Our model is established on a real physical picture and the reaction progress can be expressed in an analytic form, i.e. the reacted fraction,ξ, can be expressed analytically as a function of time, temperature, partial pressure, particle size and shape … etc. It will be greatly convenient for us to treat the effects of heating rate, particle shape and the distribution of particle size on the reacted fraction [22–24], which is difficult to be treated by current other models. For instance, if a non-isothermal reaction is considered with a constant increasing rate$\eta = \frac{T-T_0}{t}$, thus the approximate calculation formula should be [9, 10],

$$\xi = 1-\left(1-\sqrt{\left(\frac{(\sqrt{P}-\sqrt{P^{\mathrm{eq}}})}{B_{\mathrm{CP}}}\exp\left(-\frac{\Delta \mathrm{E}}{RT}\right)\right)(T-T_0)}\right)^3. \tag{16}$$

For a more accurate calculation, the formulae should be in an integration form [23]

$$\xi = 1-\left(1-\sqrt{\frac{\sqrt{P}}{B_{\mathrm{CP}}}\int_{T_0}^{T}\exp\left(-\frac{\Delta E}{RT}\right)dT+(1-(1-\xi_0)^{\frac{1}{3}})^2}\right)^3, \tag{17}$$

where $B_{\mathrm{CP}} = \frac{R^2 v_m \eta}{2D_0 k_0}$, ξ_0 is the reacted fraction at the initial temperature.

On the other hand, if the sample size has a distribution f(R), thus the reacted fraction should be [22, 24]

$$\xi = \int_{\mathrm{R1}}^{\mathrm{R2}}\left(1-\left(1-\frac{1}{R}\sqrt{\frac{t}{B_{R_0}}\exp\left(-\frac{\Delta E}{RT}\right)}\right)^3\right)\cdot \mathrm{f(R)dR} \tag{18}$$

$$B_R = \frac{1}{\frac{2K_0D_0}{v_m}(\sqrt{P}-\sqrt{P^{\mathrm{eq}}})} \tag{19}$$

here B_R is a function of P and P^{eq}. If the value of P^{eq} is very small or the temperature coefficient of P^{eq} can be neglected, thus B_R will be a constant as the oxygen partial pressure is fixed. The calculations of examples have proved that these formulae work well.

6 Conclusions

All parameters in the real physical picture model have clearly physical meanings and expressed as an analytical form that will be easy to perform a quantitative discussion, therefore, this model has intuitionistic effect in dealing with a particular kinetic problem.

This new model only requires regression once in the data fitting, as a result, this model can extract more accurate values for parameters in comparison with all other current models.

The formulae given in our model have an analytical form that will be easy to deal with the non-isothermal problem, the particle size distribution problem and the problems with various kinds of shapes. The last point is significant in our nano era.

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