Thermodynamic Model and Kinetic Compensation Effect of Spontaneous Combustion of Sulfur Concentrates

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ABSTRACT: The spontaneous combustion of the sulfur concentrate is the main hazard faced in ore storage bins. To understand the thermodynamic characteristics of spontaneous combustion of the sulfur concentrate and test whether the kinetic compensation effects are present in the spontaneous combustion process of the sulfur concentrate, typical sulfur concentrate samples were selected as the research object, and thermogravimetric experiments were carried out under an air atmosphere at heating rates of 5, 10, and 15 K/min. On this basis, the contributions of different reaction models to the mass change during the spontaneous combustion of the sulfur concentrate, as well as the thermodynamic model and kinetic compensation effect, are analyzed. The results show that solid-phase combustion contributes the most to mass loss among different mechanisms of the reaction between the sulfur concentrate and oxygen. The contributions of reaction models to mass loss are affected by the different heating rates, and the contribution of solid-phase combustion to mass loss increases with increasing heating rates. The Malek method is used to obtain the kinetic model of the spontaneous combustion of the sulfur concentrate, and its mechanism function changes from a chemical reaction model to a three-dimensional diffusion model. There is a kinetic compensation effect in the spontaneous combustion process of the sulfur concentrate, and the level of the kinetic compensation line may be one of the bases for distinguishing the spontaneous combustion tendency of the sulfur concentrate.

1. INTRODUCTION
During the mining of sulfur-bearing metals, exfoliated and accumulated sulfide ores easily oxidize in air, releasing heat, and under heat storage conditions, the ore temperature can reach the ignition point, thereby causing spontaneous combustion of sulfide ores.1−3 Sulfur concentrates are an abbreviation of selected sulfide metal ore powders. Sulfur concentrates are the granular form obtained by separating undesired components from raw sulfide metal ore (such as iron sulfide, copper sulfide, zinc sulfide, and lead sulfide) substances. The sulfur concentrates obtained after beneficiation greatly increase in chemical activity because of the increase in specific surface area. When sulfur concentrates are stacked in a mine bin for a long time, they are prone to oxidation reactions and spontaneous combustion. Spontaneous combustion of ore is the main hazard faced during the storage of sulfur concentrate and the main cause of fire in ore storage bins.1 During the spontaneous combustion of sulfur concentrate, a large number of toxic gases such as SO2 are released, which pollutants the air in the mine bin and seriously threatens the safety of workers.1 In a humid environment, a large number of acidic substances are also generated, which corrodes production equipment and facilities such as the metal doors and windows of a warehouse, grab driving, power supply lines, and electromagnetic stations and shortens their service life. During the stacking of the sulfur concentrate, agglomeration often occurs, the value of the commodity is lost, and its oxidation products are a new source of pollution for acid wastewater. The thermodynamic parameters of sulfur concentrates are important indicators reflecting their spontaneous combustion. Therefore, the thermodynamic characteristics of spontaneous combustion of sulfide ores are revealed, and the reaction kinetic parameters are further determined to provide a theoretical basis for the determination of spontaneous combustion of ore during the storage and transportation of the sulfur concentrate, which has important guiding significance for preventing spontaneous combustion of the sulfur concentrate.

Thermal analysis is a conventional method for laboratory research on fuel combustion performance and mechanisms. It
studies the reaction kinetics of solid materials under variable temperature (linear heating) conditions. Thermal analysis kinetics use the degree of fitting of different chemical reaction mechanism equations to determine the kinetic characteristics of a reaction through the change in the thermal mass loss curve. Because of its convenient operation and low sample consumption, this method is widely used in the study of physical and chemical changes of substances in various thermal environments, such as biomass combustion,6,7 coal8−11 and corrosion parameters of oil tanks,12,13 spontaneous combustion, and testing of other dynamic parameters. In recent years, the analysis of thermodynamic characteristics has become a popular topic in the study of sulﬁde ore spontaneous combustion.14 Many scholars use thermal analysis methods to determine the kinetic parameters of the oxidative decomposition of sulﬁde ores. The most common of these methods are the differential method and the integral method. Iliyas et al.15 used a kinetic simulation way to evaluate the oxidative self-heating characteristic of the sulﬁde concentrate. Yang et al.16 used thermogravimetric−differential scanning calorimetry (TG−DSC) curves to study the thermal behavior of the sulﬁde ore and used the Ozawa−Flynn−Wall method to calculate the kinetic parameters of sulﬁde ore before and after undergoing preoxidation. Li et al.17 solved the oxidation kinetic parameters of mechanically activated pyrite based on thermal analysis. Kong et al.18 evaluated the thermal behavior of the sulﬁde concentrate based on the TG−DSC technique and obtained the thermodynamic parameters from the experimental data. Liu et al.19 uncovered the thermal behavior and kinetics of the sulﬁde concentrate with TG−DTG−DSC techniques.

In a previous study, the thermal analysis of sulﬁde ore was mainly focused on a single component of the ore sample. Because the different mineral components in the ore exhibit signiﬁcant differences in the temperature and heat of oxidation, there is overlap in the various reactions, which may result in the reactions cancelling each other out so that the oxidation reaction cannot be clearly reﬂected. The endothermic and exothermic properties of the sulfur concentrate during the oxidative decomposition process should be the combined thermal properties of all minerals in the ore, not the thermal characteristics of a single component. The kinetic characteristics of sulﬁde ore during the oxidation and heating processes are

**Figure 1.** SEM photos of sulfur concentrate samples. (a) Sample A. (b) Sample B. (c) Sample C.

**Figure 2.** XRD pattern of sulfur concentrate samples. (a) Sample A. (b) Sample B. (c) Sample C.
mainly focused on the mechanism function, pre-exponential factor, activation energy, and so forth, but there are few kinetic models of sulfide ore thermal behavior and the kinetic compensation effect. At present, researchers have conducted thermal analysis on biomass chars,19 powder-activated cokes,20 coal,9 petroleum generation,21 and especially heterogeneous catalysis22 and found that there are typical dynamic compensation effects. This is a common phenomenon in many scientific fields and is important content in the study of dynamics. The existing research rarely investigates whether the same phenomenon exists in the sulfur concentrate. In fact, clarifying the oxidative kinetic model and kinetic compensation effect of the sulfur concentrate is essential for a better understanding of the spontaneous combustion behavior of sulfide ores. Therefore, we studied the thermodynamic characteristics of the sulfur concentrate through TG experiments, clarified the different thermodynamic reaction mechanisms of sulfur concentrate spontaneous combustion, and analyzed their contributions to quality changes in this paper. On this basis, the dynamic model and compensation effect of the spontaneous combustion of the sulfur concentrate are revealed. The results of the study are helpful for better understanding the complex process of spontaneous combustion of the sulfur concentrate and provide a theoretical basis for preventing the spontaneous combustion of the sulfur concentrate during storage and transportation. The rest of this paper is organized as follows. In Section 2, the research results and analysis are presented in detail, including micromorphology and crystallite structure, TG–DTG analysis, mechanism identification, contribution of gas–solid combustion to mass loss, and effect of the heating rate. In Section 3, thermodynamic characteristics are presented in detail. In Section 4, the relevant conclusions are drawn. Finally, the experiments and methods are elaborated in Section 5.

2. RESULTS AND ANALYSIS

2.1. Micromorphology and Crystallite Structure. The micromorphology and microcrystalline structure of the crushed samples were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). As shown in Figure 1, in the 5000× SEM photos of the ore samples, it can be seen that the three samples have similar structural features with blocky, sharp, and angular characteristics, and the overall structure is relatively dense, which indicates that no significant oxidation has occurred. Among them, the surface of sample B has an obvious fiber structure. Moreover, Figure 2 shows the XRD patterns of the three ore samples, and the XRD analysis results of the samples show that the main composition in the ore sample was pyrite (FeS₂), while the impurities contained in the sample were silica, dihydrate gypsum, calcium carbonate, and so forth.

2.2. TG–DTG Analysis. The TG data were directly obtained by SDT Q600 V20.9 Build 20 synchronous thermal analyzers. These data describe the quality change of the sulfur concentrate during the process of spontaneous combustion. A DTG curve is obtained by deriving the quotient of the TG curve against time, which indicates the rate of change in quality with time. The TG–DTG curves of the three samples are shown in Figure 3. It can be seen from Figure 3 that as the heating rate increases, the TG
The ore sample burns rapidly in the air and releases a large amount of SO2 in stage II. The three samples have two mass loss peaks, one of which is the largest mass loss peak, and the corresponding peak temperature is the ignition temperature of the ore sample. It can be found from the curve in Figure 3 that the ignition points are different under different heating rates. The corresponding TG curve also has two mass loss steps. Stage III is from the burnout to the stable stage (>923 K). The content of the ore samples is stable at 60–75%, and the DTG curve also tends to stabilize, but it can be found that sample B has a mass loss peak in this stage, which may be caused by a certain reaction of the impurities contained in the ore sample under high-temperature conditions.

It is worth noting that according to the DTG curve, there is no direct relationship between the maximum mass change rate and the heating rate of the three ore samples. The maximum mass loss rate of sample A decreases with the increasing heating rate, while the maximum mass loss rate of samples B and C increases with the increasing heating rate.

2.3. Mechanism Identification. From the above, it can be seen that the composition of the sulfur concentrate samples is complex, the sample reaction is composed of multiple stages, and the spontaneous combustion process is controlled by multiple dynamic reaction mechanisms. Because the TG curves are combined or overlap with each other, it is difficult to fully identify these mechanisms from the TG or DTG curves. In theory, there is an increasing period, as well as a weakening period, for each chemical reaction. Generally, the spontaneous combustion reaction of the sulfur concentrate usually starts from the chemical adsorption of the interaction between the ore and...
molecular O2. Therefore, the Gaussian function is used to fit the subpeak of the DTG curve of the three sulfur concentrate samples from the beginning of the oxidation reaction of the ore to the end of the combustion.

\[
y = y_0 + S \cdot e^{-\frac{(x-x_c)^2}{2\omega^2}} / \omega \cdot \sqrt{2\pi}  
\]

In eq 3, \(y\) represents the rate of mass change, \%/min; \(y_0\) represents the baseline of the peak (here 0); \(x\) represents the time in minutes; \(x_c\) corresponds to the peak center time; \(S\) is the peak area, \%; and \(\omega\) is the full width at half-maximum per unit time.

Sample C was taken as an example, and its DTG curves were fitted at different heating rates in stages II and III. The fitting curve is obtained, as shown in Figure 4. The corresponding subpeak parameters of the three ore samples are shown in Table 1. It can be seen from Figure 4 that the two fitted peaks are within the maximum mass loss peak, that is, there may be different mechanisms in the stage of the mass loss peak. Both peaks 1 and 2 contribute to the mass loss of the ore sample, and their strengths appear at relatively high temperatures and increase rapidly, which is attributed to the spontaneous combustion of the sulfur concentrate.

Because of the complex composition of the sulfur concentrate, the gases generated by the reaction escape during the process of thermochemical reaction. These gas phase products attached to the surface of sulfur concentrate samples are ignited, but oxygen is dispersed into the pores of the ore sample as the release intensity of the combustible gas-phase products gradually decreases and the oxidation products of the sulfur concentrate sample continue to burn. Obviously, the combustion process includes gas-phase combustion and solid-phase combustion. Comparing peak 1 and peak 2, the temperature required to produce peak 1 is lower and the reaction is rapid in this stage. Therefore, it can be inferred that gas-phase combustion occurs at peak 1, and gas-phase combustion occurs at peak 2. This shows that the main mechanism at this stage is the combustion reaction, and oxidative decomposition has little effect on it.

In addition, it can be found from Table 1 that only one peak (combustion peak) is fitted to sample A at a heating rate of 15 K/min and sample B at a heating rate of 5 K/min. The reason may be because of the influence of the impurities and different heating rates, the oxidative decomposition process of the ore sample is more complicated.

2.4. Contribution of Gas–Solid Combustion to Mass Loss. It can be seen from several sets of curve fit peaks in Figure 4 that the sulfur concentrate samples burn at different heating rates, which all result in a significant loss in quality. Therefore, the ratios of the area of subpeaks 1 and 2 were calculated to analyze the mass loss contribution of gas–solid combustion at this stage, and the specific results are shown in Figure 5 (a heating rate of 10 K/min is considered as an example). Figure 5 reflects the mass loss ratio contributed by different reaction...
mechanisms during the spontaneous combustion of the three ore samples at a heating rate of 10 K/min. The larger the ratio is, the greater the contribution of the reaction mechanism to mass loss.

When the ore samples spontaneously ignite in the air environment, peak 1 of the three sulfur concentrate samples accounts for a small proportion, which indicates that mass loss ratio contributed by gas-phase combustion is lower than that of solid-phase combustion. Because the ore sample is oxidized and decomposed in the early stage of heating, gaseous products continue to escape. For example, pyrite is separated from elemental sulfur during the initial heating, and sulfur vapor reacts with air to produce sulfur dioxide gas. As the temperature increases, the sulfur concentrate continues to release sulfur dioxide gas and generate other oxidation products. At this time, the ore sample gradually becomes a porous mixture under various chemical reactions. For sample B, the proportions of peaks 1 and 2 are similar, indicating that the effects of two kinds of the combustion phase on the mass loss are relatively balanced. This situation may be related to a large number of impurities such as active sulfur contained in sample B. Compared with sample B, samples A and C both have large proportions of peak 2, indicating that the solid-phase combustion mechanism plays a major role during mass loss, and the reactions of eqs 8 and 9 occur at this stage.

2.5. Effect of Heating Rate. Table 1 shows that the heating rate has a certain effect on the peak area, indicating that the heating rate affects the spontaneous combustion process of the sulfur concentrate. To understand the effect of the different heating rates on the spontaneous combustion process of the sulfur concentrate, a bar chart is used to describe the mass loss ratio of ore samples with different peaks (see Figure 6).

Figure 6 shows the proportions of the areas of peaks 1 and 2 of the ore sample at different heating rates, revealing the changes in the areas of different peaks in the spontaneous combustion process of the sulfur concentrate at this stage with the heating rate. It can be seen from Figure 6 that at a higher heating rate, the contribution of peak 1 is lower and that of peak 2 is higher. This occurs because at a higher heating rate, the thermal decomposition time of the ore sample is shortened, and the amount of gas released is reduced, which results in a reduction in the mass loss contribution of gas-phase combustion. Because of the high heating rate, the chemical reaction speed of the ore sample is accelerated, which causes the sulfur concentrate to directly enter the solid phase combustion stage. However, the situation of sample B is the opposite of that of the other samples. At a higher heating rate, the contribution of peak 1 is greater than that of peak 2. This may be caused by the rapid decomposition of the active sulfur component precipitated in the ore sample at a certain high temperature.

3. THERMODYNAMIC CHARACTERISTICS

3.1. Thermodynamic Model. Generally, the heating rate has little effect on the kinetic model, so the multiple heating rate method can be used to solve the apparent activation energy. The thermodynamic model of the spontaneous combustion of the
sulfur concentrate is specifically explained by the thermal analysis curve obtained when the heating rate is 10 K/min. From the previous analysis, stage II is the main mass loss stage in the entire process of spontaneous combustion of sulfur concentrate samples. It can be seen from Figure 3 that there are two mass loss peaks (II-1, II-2) in this stage, that is, there are two rapid reaction stages, and their temperature ranges are 670–770 K and 800–950 K, respectively. The kinetic modes of stages II-1 and II-2 can be determined by the Malek method, as shown in Figure 7.

**Table 2. Kinetic Model of Three Samples**

| ore sample | reaction stage II-1 | reaction stage II-2 |
|------------|---------------------|---------------------|
|            | mode                | integral function   | mode                | integral function   |
| sample A   | chemical reaction, n = 1 | −ln(1 − α)         | three-dimensional diffusion | [1 − (1 − α)1/3]5 |
| sample B   | chemical reaction, n = 12 | [(1 − α)−12 − 1)/11 | three-dimensional diffusion | [1 − (1 − α)1/3]5 |
| sample C   | chemical reaction, n = 8 | [(1 − α)−7 − 1)/7 | three-dimensional diffusion | [1 − (1 − α)1/3]5 |

Figure 7. Thermodynamic models determined through the Malek method. (a) Sample A. (b) Sample B. (c) Sample C.
For stage II-1, the test values of the two ore samples of B and C are close to the theoretical value of function 17 in Table 2, and the shape of the test curve of ore sample A matches the theoretical value of function 18. However, the reaction mechanisms represented by functions 17 and 18 are all chemical reaction mechanisms. The reaction mechanism of sample A is considered to be a chemical reaction when the reaction order $n = 1$, and the kinetic model is the integral of the $-\ln(1 - \alpha)$ function. The reaction mechanisms of samples B and C are the chemical reaction mechanisms of reaction orders $n = 12$ and $n = 8$, respectively, and their kinetic modes are the integral function of mathematical expressions $((1 - \alpha)^{-11} - 1)/11$ and $((1 - \alpha)^{-7} - 1)/7$. The reaction order indicates the speed of the chemical reaction. The larger the order is, the faster the reaction. Samples B and C experience a violent combustion reaction in stage II-1, which results in a rapid loss of mass. The TG–DTG curve in Figure 3 can intuitively reflect this phenomenon. The mass loss rate of the sulfur concentrate at this stage reaches 25%, and the peak width of the maximum mass loss peak is narrow. In stage II-2, the test curve shapes of the three ore samples A, B, and C all match the function 4 (see Table 1). Therefore, the reaction mechanism of three sulfur concentrate samples in stage II-2 is

![Graphs showing variation in E corresponding to the change in T and that of ln A for the three ore samples (heating rate = 5 K/min). (a) Sample A. (b) Sample B. (c) Sample C.](https://dx.doi.org/10.1021/acsomega.0c02884)
three-dimensional diffusion, and their kinetic model is the integral function of mathematical expression \[1 - (1 - \alpha)^{1/3}\]. See Table 2 for details.

3.2. Kinetic Compensation Effect. It can be seen from Figure 8 that the apparent activation energy \(E\) of the three samples is positively correlated with the pre-exponential factor \(A\), and the correlation coefficients \(R\) are 0.99604, 0.98357, and 0.99686, respectively. As the temperature increases, these parameters both increase first and then decrease, indicating that there is a compensation effect between them. The kinetic compensation effect is an important component of thermodynamic analysis that exists in various systems and reaction processes. There are many reasons for the compensation effect in a kinetic process. Some researchers considered it to be caused by systematic and experimental errors, \(^{23,24}\) experimental conditions, and equipment quality. \(^{25}\) Curtis and Conner \(^{26}\) believe that the transition-state theory of heterogeneous reaction kinetics can explain the compensation effect. According to the theory of the transition state, the distance between atoms in the activated complex state is longer than the normal chemical bond, which results in the bond of the activated complex being weaker than the normal bond, but translation, rotation, and limited vibration can still be performed like in normal molecules. Spontaneous combustion of the sulfur concentrate is a typical heterogeneous reaction. During the experiment, some problems such as experimental conditions, experimental errors, and equipment quality were avoided as much as possible. Therefore, the combustion dynamics compensation effect can be explained by the transition-state theory.

During the spontaneous combustion of sulfur concentrate samples, as the temperature increases, some reactions gradually occur between the less active mineral components and oxygen, resulting in an increase in the energy required. Because of the lower activity of these mineral components and weaker binding to oxygen, the freedom of movement of the mineral—oxygen complex increases, which means that the pre-exponential factor \(A\) increases. As the reaction continues, unstable intermediate products are gradually formed, namely, activated complexes. Generally, the activation energy required for this activated complex to combine with oxygen to form \(\text{Fe}_2\text{O}_3\) and other materials is small, and the activation entropy reflected is also small, which leads to a small pre-exponential factor \(A\). In general, the spontaneous combustion reaction of sulfur concentrates shows a significant compensation effect. It can be seen from Figure 9 that the linear relationship exists between the activation energy \(E\) and the value of \(\ln A\). If the activation energy distribution trend of the spontaneous combustion reaction of the sulfur concentrate can be found, the pre-exponential factor is obtained according to its kinetic compensation effect; the same goes for the opposite.

Furthermore, the thermodynamic compensation lines for the spontaneous combustion reaction of the three ore samples are not the same, which may be related to the differences in the structure and stability of the active components of the three ore samples and the intermediate products of the spontaneous combustion process. As shown in Figure 9, sample B has the highest compensation effect line, followed by sample C, and sample A has the lowest, which may indicate that greater the component activity of the ore sample is, the higher the kinetic compensation effect line for the spontaneous combustion process. Therefore, the level of the compensation effect line may be used as the basis for distinguishing the spontaneous combustion tendency of the sulfur concentrate.

4. CONCLUSIONS

Spontaneous combustion is the main hazard during the storage of sulfur concentrates, and it is also the main cause of fire in ore storage bins and air pollution in the working environment. The thermodynamic model and compensation effect of the spontaneous combustion process of the sulfur concentrate are analyzed based on TG experiments, and some conclusions are obtained as follows:

1. During the spontaneous combustion process, the sulfide ore sample is mainly divided into three stages: the water evaporation stage, the main mass loss stage, and the burnout stable stage. The high heating rate is conducive to the pyrolysis of the sulfur concentrate sample, and the TG—DTG curve has a tendency to move toward high temperatures with increasing temperature. In the main mass loss stage, solid-phase combustion contributes more to the quality loss of the sulfur concentrate.

2. The thermodynamic reaction mechanism changes significantly at the main mass loss stage of the spontaneous combustion process. For all of sulfur concentrate samples used in this study, the kinetics and mechanism of the reactions are converted into a three-dimensional diffusion model based on the chemical reaction mechanism. The same reaction mechanism occurs in the same stage in the spontaneous combustion process of the ore samples, but the thermodynamic modes of the different ore samples are not completely consistent.

3. During the spontaneous combustion process of the sulfur concentrate, the variation in \(E\) is consistent with the change in \(A\), which means that there is a kinetic compensation effect in the reaction process, and the level of the compensation effect line may be used as the basis for distinguishing the spontaneous combustion tendency of the sulfur concentrate.

5. EXPERIMENTS AND METHODS

5.1. Sample Preparation. The sulfur concentrate samples used in the experiment were collected from three ore storage bins in a pyrite mining area of Guangdong Province and were numbered sample A, sample B, and sample C. Because of the high environmental humidity of the original ore storage bins,
some samples have high water contents. For this reason, the samples were placed in a vacuum drying oven and dried at 333 K for 24 h. Then, the samples were manually crushed, sieved in a −300 mesh (approximately 50 μm) and placed in a drying cabinet before the experiment. The particle size distributions are shown in Figure 10. The particle size distributions of the three samples are basically uniform.

5.2. Experimental Equipment and Conditions. The SDT Q600 V20.9 Build 20 synchronous thermal analyzer from the TA company was used in the experiment. The mass of the sample measured in each test was approximately 10 mg, and the sample was placed in the crucible. The heating rates were set to 5, 10, and 15 K/min. The combustion temperature ranged from room temperature to 1250 K. The experimental combustion atmosphere was simulated in the air state. To maintain the dynamic atmosphere of the thermal reaction and avoid false mass gain of the sample due to air flow, the air flow rate was controlled to 40 mL·min⁻¹.

5.3. Thermodynamic Methods. 5.3.1. Thermodynamic Theory. In the air environment, the spontaneous combustion of the sulfur concentrate is a typical gas–solid reaction. According to thermal analysis kinetic theory, its reaction rate can be expressed by eq 4:

\[
\frac{da}{dt} = A e^{-E/(RT)} f(\alpha)
\] (4)

In eq 1: \(\alpha\) is the conversion rate of the oxidative decomposition reaction of the sulfur concentrate, and \(\alpha = (m_0 - m_t)/(m_0 - m_\infty)\), where \(m_0\) denotes the mass at the initial time, \(m_t\) denotes the mass at time \(t\), and \(m_\infty\) is the reaction termination mass at time \(t\); \(t\) denotes the reaction time, \(s\); \(T\) denotes the reaction temperature, K; \(A\) denotes the pre-exponential factor, s⁻¹; \(E\) denotes the apparent activation energy, kJ/mol; and \(R\) denotes the molar gas constant, with a value of 8.134 J·mol⁻¹·K⁻¹; and \(f(\alpha)\) is a function of the oxidation reaction mechanism of the sulfur concentrate. The Coats–Redfern method was used to process eq 4, and the heating rate \(\beta = dT/dt\) was substituted into eq 4 to obtain eq 5

\[
\frac{da}{f(\alpha)} = \frac{A}{\beta} e^{-E/(RT)} dT
\] (5)

Equation 5 reflects the relationship between the mass consumption and reaction rate.

5.3.2. Inference Method of the Thermodynamic Model. Multiple reaction stages are involved during the spontaneous combustion process of the sample, and each stage has an independent reaction equation. The thermodynamic parameters of each stage are constant, and the total mass loss is equal to the sum of the mass losses of each stage. The Malek method is used to infer the dynamic model from the function \(y(\alpha)\)

\[
y(\alpha) = \left(\frac{T}{T_{0.5}}\right)^2 \cdot \frac{(da/dt)}{(da/dt)_{0.5}} = \frac{f(\alpha) \cdot G(\alpha)}{f(0.5) \cdot G(0.5)}
\] (6)

\[
f(\alpha) = \frac{1}{dG(\alpha)/d\alpha}
\] (7)

where \(\alpha\) denotes the conversion rate and \(y(\alpha)\) denotes the characteristic function defined to find kinetic model and parameters; \(T\) denotes the absolute temperature, K; \(T_{0.5}\) corresponds to temperature at \(\alpha = 0.5\); \(f(\alpha)\) denotes the differential form of the reaction function; \(G(\alpha)\) denotes the
integral form of the reaction function; \( \frac{dG}{dt} \) is the reaction rate; and \( \left( \frac{dG}{dt} \right)_{0, \alpha} \) denotes the reaction rate corresponds to \( \alpha = 0.5 \). When the test value is close to the theoretical value, the corresponding mechanism function is considered to represent the thermodynamic model. The common thermodynamic models are described by Li et al.\(^9\) However, some functions such as function 7–12, function 1 and function 19–23\(^9\) have the same theoretical curve. Therefore, the Popescu method\(^28\) was used to initially screen the mechanism functions that meet the requirements. Popescu\(^29\) described an integral method of analyzing the thermodynamic and reaction mechanisms by using the conversion rates measured at the same temperatures on the TG curves. Therefore, Eq 8 is obtained by integrating the basic equations of the reaction kinetics.

\[
G(\alpha)_{\text{m,n}} = \int_{\alpha_n}^{\alpha_m} \frac{d\alpha}{f(\alpha)} = \frac{1}{\beta} \int_{T_n}^{T_m} k(T)\,dT = \frac{1}{\beta} \int_1^{I(T)_{\text{m,n}}} 
\]

where \( T_m \) and \( T_n \) denote the temperatures corresponding to stage-m and stage-n, respectively; \( K \); \( \alpha_n \) and \( \alpha_m \) denote the conversion rates corresponding to \( T_m \) and \( T_n \); \( k(T) \) denotes the reaction rate, 1/min; and \( \beta \) denotes the heating rate, K/min. Reasonable \( G(\alpha) \) will make its relation with \( 1/\beta \) pass through the origin.

5.3.3. Research Methods for Kinetic Compensation Effects.

The Kissinger–Akahira–Sunose method\(^29\) was used to calculate the \( E \) value of three samples during spontaneous combustion

\[
\ln(\beta/T^2) = \ln \left( \frac{A \cdot R}{E \cdot G(\alpha)} \right) - \frac{E}{R \cdot T} 
\]

If variation is in \( E \) with the change in \( A \), there is a kinetic compensation effect in the gas–solid surface reaction and a linear relationship exists between \( E \) and \( \ln A \), as follows

\[
\ln A = a \cdot E + b 
\]

where \( a \) is the slope, \( b \) is the intercept, \( a \) and \( b \) are compensation parameters, and \( E \) is obtained from the linear relationship between \( \ln(\beta/T^2) \) and \( 1/T \). Equation 10 indicates that the pre-exponential factor \( A \) gets partial compensation for the effect of apparent activation energy \( E \) change.\(^{20}\)

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**Notes**

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