A New Kinetic Method of Processing TA Data

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A new method of investigating the kinetic parameters and mechanism functions of a solid phase reaction is presented. This method is to analyze the data based on the use of these data at the same temperature and the same degree of conversion on a series of TA curves with different heating rates, so that the kinetic triplet—the activation energy E, the pre-exponential factor A and the analytical form of the function of conversion $f(\alpha)$ can be obtained. The main advantage of this method is that the values of E and $f(\alpha)$ are obtained respectively, and the determination of $f(\alpha)$ is not under the influence of the value of E and the calculation of the value of E is not influenced by the $f(\alpha)$ either.

Keywords   new method, thermal analysis, kinetics, the function of conversion, activation energy

Introduction

In the field of TA, there are many kinetic model functions and the corresponding processes to describe the most probable mechanism function of a solid phase reaction. They are usually classified as differential and integral methods mathematically, and single scan method and multiple scan method operationally. Single scan method can compute all kinetic parameters through the analysis of one single TA curve. For a long time, it has been regarded as a strength of TAK. But, recent researches have found that the results obtained from the same experiment using this method were not consistent even under the strict experimental conditions. So the scientific quality of this method is doubted.[1-3] In addition, it has also been found that in terms of the thermal decomposition mechanism of a solid phase reaction, multiple scan methods (covering some iso-conversional methods) are the most effective ones to deal with data.[4]

Based on the iso-conversional[5] and the variant iso-conversional methods,[6] the present paper proposes a new method of investigating the kinetics and mechanisms of a solid phase reaction by using data obtained from a series of TA curves at the same temperature and the same degree of conversion. In this way, the kinetic triplet can be obtained, *i.e.*, the activation energy E, the pre-exponential factor A and the conversion function $f(\alpha)$. According to its characteristics, the method is named double equal-double steps method. The proposed method has been tested for a simulated reaction on data given in the literatures. In the case of the data from the literatures the calculated results are in excellent agreement with those used for simulation. It has to be stressed that the method is fit for the single step reaction whose activation energy E or mechanism functions $f(\alpha)$

do not change along with the degrees of conversion. The advantage of the proposed method is that the activation energy E and the conversion function $f(\alpha)$ are obtained respectively, and the determination of mechanism function is not under the influence of the value of E and the value of E is not under the influence of the mechanism functions either.

Theory

We proposed a new method of processing the data of thermal analysis kinetics, whose steps are as follows.

Determination of the function of conversion

Flynn-Wall-Ozawa equation[5] is as follows:

$$\log \beta = \log\left(\frac{AE}{RG(\alpha)}\right) - 2.315 - 0.4567\frac{E}{RT} \qquad (1)$$

Eq. (1) is changed into:

$$\log G(\alpha) = \log\left(\frac{AE}{R}\right) - 2.315 - 0.4567\frac{E}{RT} - \log \beta \qquad (2)$$

where $G(\alpha)$ is the integral mechanism function, T the absolute temperature, A the pre-exponential factor, R the gas constant, E the apparent activation energy and β the linear heating rate. By substituting the values of conversion degrees at the same temperature on several TA curves, the different mechanism functions $G(\alpha)$ and various heating rates into Eq. (2), the linear correlation coefficient r, the slope b and the intercept a at different

temperatures were obtained by the linear least squares method with log $G(\alpha)$ versus log β. If the linear correlation coefficient r is the best and the slope approaches -1, the relevant function under such conditions is the probable mechanism function of a solid phase reaction. So various common conversion functions are listed in Table 1.

Calculation of E and A

By substituting the values of temperatures at the same degree of conversion, heating rates and the conversion function $G(\alpha)$ determined above in Eq. (1), the linear correlation coefficient r, the slope b and the intercept a at the different conversion degrees were obtained by the linear least squares method with log β versus $1/T$. From the value of the slope about the plot, E can be calculated. From the value of the intercept, A can be also calculated.

Experimental

The experimental data used in the new method were derived from the published in the literatures.[6,7]

Results and discussion

Determination of $f(\alpha)$ and $G(\alpha)$

The values of conversion degrees at the same temperature on seven TA curves in the literatures[6,7] are listed in Table 2.

By substituting the values of α, β and nine conversion functions $G(\alpha)$ in Table 1 into Eq. (2), the linear correlation coefficient r, the slope b and the intercept a at the different temperatures were obtained by the linear least squares method with log $G(\alpha)$ versus log β which are listed in Table 3.

From Table 3, it can be easily seen that only the coefficient r of the function $G(\alpha) = -\ln(1-\alpha)$ is the best and its slope approaches -1, so the probable mechanism function is $G(\alpha) = -\ln(1-\alpha)$, $f(\alpha) = 1-\alpha$. One can notice that the results obtained by the proposed method are in good agreement with those in literatures.[6,7]

Calculation of E and A

The values of temperatures at the same degree of conversion on seven TA curves in the literatures[6,7] are listed in Table 4.

By substituting the values of α, β, T and conversion functions $G(\alpha) = -\ln(1-\alpha)$ into Eq. (1), the linear correlation coefficient r, the slope b and the intercept a at the different conversion degrees were obtained by the linear least squares method with log β versus $1/T$. The activation energy E can be calculated from the value of the slope and the pre-exponential factor A can also be calculated from the value of the intercept. The results are listed in Table 5.

It can be easily seen that the results in Table 5 are in good agreement with those in literatures.[6,7]

Table 1 Kinetic functions of $f(\alpha)$ and $G(\alpha)$ used for the present analysis[6]

Mechanism (code)	$f(\alpha)$	$G(\alpha)$
Avrami-Erofee ($m=2, 3, 4$) (Code: AE2, AE3, AE4)	$(1-\alpha)[-\ln(1-\alpha)]^{1/m}$	$m[-\ln(1-\alpha)]^{1/m}$
Diffusion mechanism: (D1)	α^{-1}	$1/2\alpha^2$
(D2)	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
(D3)	$[1-(1-\alpha)^{1/3}]^{-1}(1-\alpha)^{2/3}$	$3/2[1-(1-\alpha)^{1/3}]^2$
Ginstling-Brounshtein (D4)	$[(1-\alpha)^{-1/3}-1]^{-1}$	$3/2[1-2\alpha/3-(1-\alpha)^{2/3}]$
Reaction order (R) $n=1$	$1-\alpha$	$-\ln(1-\alpha)$
$n \neq 1$	$(1-\alpha)^n$	$[1-(1-\alpha)^{1-n}]/(1-n)$

Table 2 The values of conversion degrees at the same temperature but different heating rates[6,7]

Temp./K	α						
	$\beta=1$ K•min^{-1}	$\beta=2$ K•min^{-1}	$\beta=5$ K•min^{-1}	$\beta=10$ K•min^{-1}	$\beta=20$ K•min^{-1}	$\beta=50$ K•min^{-1}	$\beta=100$ K•min^{-1}
336.245	0.65093	0.41006	0.19220	0.10000	—	—	—
344.346	0.89114	0.67195	0.36213	0.20000	0.10747	—	—
352.535	—	0.90000	0.60187	0.37090	0.20660	0.08100	—
362.363	—	—	0.87502	0.65092	0.41000	0.19219	0.1000
367.602	—	—	0.80000	0.55325	0.27785	0.1558

TA data

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Table 3 The results from the linear least squares method at different temperatures

T/K	Mechanism (code)	a	b	r
	AE2	0.3126	−0.4990	−0.9999
	AE3	0.4848	−0.3327	−0.9999
	AE4	0.6078	−0.2495	−0.9999
	D1	−0.6306	−1.6308	−0.9977
336.245	D2	−0.5153	−1.7408	−0.9989
	D3	−0.8641	−1.8660	−0.9997
	D4	−0.9498	−1.7824	−0.9992
	R (n=1)	**0.0231**	**−0.9980**	**−0.9999**
	R (n=0.5)	−0.0747	−0.9021	−0.9994
	AE2	0.4739	−0.4967	−0.9999
	AE3	0.5924	−0.3311	−0.9999
	AE4	0.6885	−0.2483	−0.9999
	D1	−0.2905	−1.4285	−0.9917
344.346	D2	−0.0997	−1.5800	−0.9959
	D3	−0.3403	−1.7750	−0.9991
	D4	−0.4990	−1.6440	−0.9972
	R (n=1)	**0.3458**	**−0.9933**	**−0.9999**
	R (n=0.5)	0.1606	−0.8396	−0.9979
	AE2	0.6404	−0.5111	−0.9997
	AE3	0.7034	−0.3407	−0.9997
	AE4	0.7718	−0.2555	−0.9997
	D1	0.2130	−1.5034	−0.9861
352.535	D2	0.4463	−1.6491	−0.9923
	D3	0.2626	−1.8381	−0.9975
	D4	0.0656	−1.7110	−0.9944
	R (n=1)	**0.6788**	**−1.0221**	**−0.9997**
	R (n=0.5)	0.4481	−0.8726	−0.9955
	AE2	0.8088	−0.4974	−0.9999
	AE3	0.8156	−0.3316	−0.9999
	AE4	0.8559	−0.2487	−0.9999
	D1	0.7267	−1.4681	−0.9917
362.363	D2	1.0088	−1.6119	−0.9957
	D3	0.8801	−1.7936	−0.9989
	D4	0.6464	−1.6716	−0.9971
	R (n=1)	**1.0156**	**−0.9947**	**−0.9999**
	R (n=0.5)	0.7433	−0.8521	−0.9977
	AE2	0.8924	−0.4897	−0.9999
	AE3	0.8713	−0.3265	−0.9999
	AE4	0.8977	−0.2449	−0.9999
	D1	0.9886	−1.4323	−0.9963
367.602	D2	1.2989	−1.5818	−0.9984
	D3	1.1939	−1.7646	−0.9998
	D4	0.9448	−1.6421	−0.9990
	R (n=1)	**1.1827**	**−0.9794**	**−0.9999**
	R (n=0.5)	0.8943	−0.8373	−0.9993

Table 4   Temperatures corresponding to the same degree of conversion at different heating rates[6,7]

α	T/K						
	$\beta=1$ K•min^{-1}	$\beta=2$ K•min^{-1}	$\beta=5$ K•min^{-1}	$\beta=10$ K•min^{-1}	$\beta=20$ K•min^{-1}	$\beta=50$ K•min^{-1}	$\beta=100$ K•min^{-1}
0.1	313.549	320.062	329.085	336.245	343.715	354.097	362.363
0.4	328.774	335.921	345.845	353.738	361.988	373.482	382.657
0.8	340.773	348.441	359.105	367.602	376.497	388.913	398.844
0.9	344.694	352.535	363.447	372.146	381.257	393.984	404.170

Table 5   The values of the kinetics parameters computed by the Flynn-Wall-Ozawa method

α	$E/(\text{kJ•mol}^{-1})$	$A \times 10^{12}/\text{s}^{-1}$	r
0.1	84.87	1.4927	−0.9999
0.4	85.14	1.6389	−0.9999
0.8	85.34	1.7579	−0.9999
0.9	85.41	1.7978	−0.9999

Conclusions

A new method was proposed for investigating kinetic parameters and mechanism functions of a solid phase reaction. It is based on the data acquired for a reaction investigated under various heating rates and may be considered as a new multiple scan method. Its main advantage is that the value of the activation energy E and the function of conversion $f(\alpha)$ are obtained respectively, and what's more, the determination of mechanism function is not under the influence of the value of E, and the value of E is not under the influence of the mechanism functions either.

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Correction statement

There is something wrong on the molecular frame (Figure 1) in the page 1143 in the Chinese Journal of Chemistry (2004). Because it should be two ester groups between the two long alkyl chains and 1-, or 2-carbon atoms in glycerol backbone, on the glycerol backbone, the 1-, and 2-carbon atoms need to add two oxygen atoms to connect with the two carbonyl groups of long alkyl chains respectively.