Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 463-475

CALORIMETRIC REACTION RATE DETERMINATION WITH THE CHARACTERISTIC KINETIC PARAMETER METHOD

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Abstract

On the basis of the theory of thermokinetics proposed in the literature, a novel thermokinetic method for determination of the reaction rate, the characteristic parameter method, is proposed in this paper. Mathematical models were established to determine the kinetic parameters and rate constants. In order to test the validity of this method, the saponifications of ethyl benzoate, ethyl acetate and ethyl propionate, and the formation of hexamethylenetetramine were studied with this method. The rate constants calculated with this method are in agreement with those in the literature, and the characteristic parameter method is therefore believed to be correct.

In the light of the characteristic parameter method, we have developed further two thermo-kinetic methods, the thermoanalytical single and multi-curve methods, which are convenient for simultaneous determination of the reaction order and the rate constant. The reaction orders and rate constants of the saponifications of ethyl acetate and ethyl butyrate and the ring-opening reaction of epichlorohydrin with hydrobromic acid were determined with these methods, and their validity was verified by the experimental results.

Keywords: characteristic parameter method, reaction order, simple-order reactions, thermokinetic research method

Introduction

The thermoanalytical curve of a chemical reaction implies kinetic and thermodynamic information on the reaction. It is an important goal of thermokinetics to establish a research method to obtain such valuable information. On the basis of the fundamental theory of thermokinetics, the dimensionless parameter method of different-order reactions was earlier developed [1–4]. However, it can not be applied to those reactions whose ratio of the characteristic thermoanalytical curve data α_m^*/A is below the critical value. Additionally, reactions of different orders involve different forms of the dimensionless parameter method, which is inconvenient for the users.

In order to enrich and improve thermokinetic research, a novel research method for simple-order reactions, the characteristic parameter method, is suggested in this paper.

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1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

It can be used to determine not only the rate constant, but also the reaction order of the studied reaction. Its validity is tested by comparison with experimental results.

Theory and method

Thermokinetic characteristic equation of chemical reaction

In a previous article [5], we proved that the thermokinetic equations of a chemical reaction taking place in a batch conduction calorimeter can be described as

$$\frac{G\alpha^* - \Lambda\Delta}{G\alpha_\mathrm{T}} = F(t) \tag{1}$$

$$\frac{G\Delta + \Lambda\left(\frac{\mathrm{d}\Delta}{\mathrm{d}t}\right)}{G\alpha_\mathrm{T}} = G(t) \tag{2}$$

where $\alpha*$ is the peak area after time t, Δ is the peak height at time t and α_T is the total area under the curve. G and Λ are the coefficient of heat loss and the effective capacity of the calorimetric system, respectively. $F(t)$ and $G(t)$ are functions with respect to time t. For different reaction orders, $F(t)$ and $G(t)$ have different expressions (as shown in Table 1).

With the definition $\beta=G/\Lambda$, which is generally called the cooling constant of a thermokinetic system, we have

$$\frac{\alpha^*}{\alpha_\mathrm{T}} - \frac{\Delta}{\beta\alpha_\mathrm{T}} = F(t) \tag{3}$$

$$\frac{\Delta}{\alpha_\mathrm{T}} + \frac{\frac{\mathrm{d}\Delta}{\mathrm{d}t}}{\beta\alpha_\mathrm{T}} = G(t) \tag{4}$$

We let

$$\Phi = \frac{Q_\infty - Q}{Q_\infty} \tag{5}$$

where Φ is the ratio of the heat effect produced at time t and the total heat effect, whose value implies the extent of reaction. According to the Tian equation [6], it can be proved that

$$\Phi = \frac{\alpha^*}{\alpha_\mathrm{T}} - \frac{\Delta}{\beta\alpha_\mathrm{T}} \tag{6}$$

Table 1 Expressions for $F(t)$ and $G(t)$ of reactions with different orders*

Reaction type	$F(t)$	$G(t)$
First-order reaction	$\mathrm{e}^{-k_1 t}$	$k_1 \mathrm{e}^{-k_1 t}$
Second-order reaction with equal concentrations	$\frac{1}{1+K_2 t}$	$\frac{K_2}{(1+K_2 t)^2}$
Second-order reaction with unequal concentrations	$\frac{R_c-1}{R_c \mathrm{e}^{K_2' t}-1}$	$\frac{R_c(R_c-1)K_2' \mathrm{e}^{K_2' t}}{(R_c \mathrm{e}^{K_2' t}-1)^2}$
n^{th}-order reaction with equal concentrations	$\frac{1}{[1+(n-1)K_n t]^{1/(n-1)}}$	$\frac{K_n}{[1+(n-1)K_n t]^{n/(n-1)}}$

*$K_2=k_2C_o$; $K_2'=k_2(A_o-B_o)$; $K_n=k_nC_o^{n-1}$; $n\neq1$. A_o, B_o and C_o are the initial concentrations of the reactants, and R_c is the ratio of the concentrations of the reactants (A_o/B_o)

In the following, t_m is the time corresponding to the maximum peak height of the thermoanalytical curve, generally called the characteristic time parameter. When $t=t_m$, then $\Phi=\Phi_m$, $d\Delta/dt=0$, $F(t)=F(t_m)$ and $G(t)=G(t_m)$. From Eqs (3), (4) and (6), we obtain the thermokinetic characteristic equations of reactions with simple order:

$$\Phi_m = F(t_m) \tag{7}$$

$$\frac{\Delta_m}{\alpha_T} = G(t_m) \tag{8}$$

Mathematical models of the characteristic parameter method for simple-order reactions

According to the expressions for $F(t)$ and $G(t)$ listed in Table 1, from Eqs (7) and (8), it can be proved that for a first-order reaction:

$$k_1 = \frac{\dfrac{\Delta_m}{\alpha_T}}{\Phi_m} \tag{9}$$

for an *n*th-order reaction with equal concentrations:

$$K_n = \frac{\dfrac{\Delta_m}{\alpha_T}}{\Phi_m^n} \tag{10}$$

and for a second-order reaction with unequal concentrations:

$$K_2' = \frac{\dfrac{\Delta_m}{\alpha_T}}{\Phi_m + \Phi_m^2(R_c - 1)} \tag{11}$$

Equations (9)–(11) are the formulae for calculating the kinetic parameters for simple-order reactions when using the characteristic parameter method. From the thermoanalytical curve, we know the values of Δ_m , t_m and α_T. The kinetic parameter and rate constant of the studied reaction can therefore be conveniently calculated.

Simultaneous determination of the reaction order and the rate constant

For an irreversible reaction:

$$aA + bB + cC \rightarrow P \tag{12}$$

where A, B and C are reactants, a, b and c are the stoichiometric numbers of molecules A, B and C, respectively, and P is the product.

Let us suppose that the rate law for Eq. (12) can be expressed as

$$\nu = k_n[A]^{n_a}[B]^{n_b}[C]^{n_c} \tag{13}$$

where ν is the rate of the chemical reaction, $[A]$, $[B]$ and $[C]$ are the concentrations of A, B and C, respectively, and n_a, n_b and n_c are the reaction orders with respect to A, B and C, respectively.

The total order of the reaction is given by

$$n = n_a + n_b + n_c \tag{14}$$

Let us suppose that there is effectively constant concentration of all components except one, which for convenience is taken as component A, so that we have a pseudo-n_ath-order reaction. Then, during a reaction run, $[B]$ and $[C]$ and their powers may be lumped in with the rate constant k_n to form a pseudo-n_ath-order rate constant k', which is given by

$$k' = k_n[B]_o^{n_b}[C]_o^{n_c} \tag{15}$$

where $[B]_o$ and $[C]_o$ are the initial concentrations of B and C, respectively. Thus:

$$\nu = k'[A]^{n_a} \tag{16}$$

This can be treated as an n_ath-order reaction with equal concentrations.

On the basis of the characteristic parameter method in the present paper, the single and multi-thermoanalytical curve methods for determination of the reaction order and the rate constant can be developed as follows.

Thermoanalytical single-curve method

When $t=t_m$ and t_i, from Eqs (3) and (6) and the expression of the nth-order reaction with equal concentrations listed in Table 1, we obtain

$$\Phi_m^{1-n_a} = 1 + (n_a - 1)K_{n_a}t_m \tag{17}$$

$$\Phi_i^{1-n_a} = 1 + (n_a - 1)K_{n_a}t_i \tag{18}$$

From Eqs (17) and (18), we have

$$\Phi_i^{1-n_a} = \Phi_m^{1-n_a}\left[1 + \frac{(n_a - 1)(t_i - t_m)\Delta_m}{(\Phi_m\alpha_T)}\right] \tag{19}$$

Equation (19) is the mathematical expression of the thermoanalytical single-curve method. The values of Φ_m, Φ_i, Δ_m, α_T, t_i and t_m can be obtained from one thermoanalytical curve, and therefore Eq. (19) involves only one unknown reaction order, n_a, which can easily be calculated. k' can then be calculated as

$$k' = (\Phi_i^{1-n_a} - \Phi_m^{1-n_a})\frac{[A]_o^{1-n}}{(n_a - 1)(t_i - t_m)} \tag{20}$$

In principle, n_b and n_c can be obtained in the same way as n_a, and can also be obtained by the following procedure.

Under the pseudo-nth-order condition, let $[B]_o$ be varied but let $[C]_o$ be constant. Then, from Eq. (15), we have

$$k_1' = k_n[B]_{o1}^n[C]_o^n \tag{21}$$

$$k_2' = k_n[B]_{o2}^n[C]_o^n \tag{22}$$

From Eqs (21) and (22), it can be proved that

$$n_b = \frac{\log\left(\frac{k_1'}{k_2'}\right)}{\log\left(\frac{[B]_{o1}}{[B]_{o2}}\right)} \tag{23}$$

where k_1' and k_2' are the rate constants when the initial concentrations of B are $[B]_{o1}$ and $[B]_{o2}$, respectively.

Equation (19) can not be applied to the first-order reaction. According to the formula of F(t) for a first-order reaction and Eqs (3) and (6), we have

$$\ln\Phi = -k_1 t \tag{24}$$

Equation (24) is characteristic of a first-order reaction. If plots $\ln\Phi$ *vs.* t exhibit a good linear relationship, then the reaction studied is a first-order reaction.

n_c can be obtained in the same way as n_b, and thus the total reaction order n can be obtained via Eq. (14).

Thermoanalytical multi-curve method

Under the pseudo-n_ath-order condition, according to the relationship between kinetic parameter K_n and rate constant k_n, and from Eq. (10), we have

$$\frac{\Delta_m[A]_o}{\alpha_T} = k'(\Phi_m[A]_o)^{n_a} \tag{25}$$

The logarithmic form of Eq. (25) is

$$\log\left(\frac{\Delta_m[A]_o}{\alpha_T}\right) = \log k' + n_a\log(\Phi_m[A]_o) \tag{26}$$

If $[B]_o$ and $[C]_o$ are kept constant during the experimental runs, then k' is constant. A plot of $\log(\Delta_m[A]_o/\alpha_T)$ *vs.* $\log(\Phi_m[A]_o)$ should give a straight line of slope n_a.

In practice, it is possible in this way to obtain the reaction order with respect to each reactant by making each one successively the least concentrated component. Thus, the total order n can also be obtained.

It is easy to find the rate constant k_n by the characteristic parameter method after n_a, n_b and n_c have been determined.

Experimental

Reaction system

In order to test the validity of the characteristic parameter method in this paper, the thermokinetics of four reactions with different orders, as shown below, have been studied:

1. A pseudo-first-order reaction: the saponification of ethyl benzoate in aqueous ethanol as solvent at 25°C.
2. A second-order reaction with unequal concentrations: the saponification of ethyl propionate in aqueous ethanol as solvent at 30°C.
3. A second-order reaction with equal concentrations: the saponification of ethyl acetate in aqueous solution at 30°C.
4. A third-order reaction: the reaction of formaldehyde with ammonia in aqueous solution to form hexamethylenetetramine at 20°C.

All the reagents in the above reactions were analytically pure reagents. The concentrations of NaOH and KOH in solution were standardized with potassium hydrogen phthalate.

Measurement of thermoanalytical curves

All the thermoanalytical curves for the reaction systems mentioned above were measured with a twin conduction calorimeter, whose basic construction was similar to that of the Calvet calorimeter [7]. Two equal systems (reaction cell and reference cell) were placed in an isothermal block and thermopiles were situated between the measuring system and the block according to the twin principle. When a chemical reaction took place in the calorimeter, the output signal was recorded after it was amplified.

Results and discussion

Determination of the cooling constant of a thermokinetic system

The cooling constant of a thermokinetic system is an important parameter in our method. Its value must be determined by using electric calibration [8]. When a heat process with constant electric power is taking place in a vessel containing the terminal reaction solution of the calorimeter, the heat curve is recorded. When heating is stopped, the cooling curve can be obtained, from which the cooling constant can

Table 2 The cooling constant k determined by using electric calibration

Reaction system	$k \cdot 10^3$/ s^{-1}
Saponification of ethyl benzoate	1.92
Saponification of ethyl propionate	2.04
Saponification of ethyl acetate	1.86
Formation of hexamethylenetetramine	1.85
Saponification of ethyl butyrate	2.12
Ring-opening reaction of epichlorohydrin	1.50

Table 3 Thermoanalytical curve data and rate constants for saponification of ethyl benzoate at 25°C (solvent: 50% (v/v) $EtOH–H_2O$; $C_o(NaOH)=0.046$ mol l^{-1})

C_o(ester)/ mol l^{-1}	Δ_m/ mm	$10^{-4} \cdot \alpha_m$/ mm s	$10^{-4} \cdot \alpha_T$/ mm s	Φ_m	$10^4 \cdot k_1^*$/ s^{-1}	$10^3 \cdot k_2$/ l mol^{-1} s^{-1}
0.451	29.5	6.49	8.40	0.590	5.95	1.32
0.451	30.8	6.85	8.79	0.597	5.87	1.30
0.558	38.2	7.15	9.41	0.548	7.41	1.33
0.558	38.0	7.14	9.44	0.547	7.36	1.32
0.658	46.8	7.90	10.5	0.520	8.57	1.30
					Average:	1.31
					Literature value [9]:	1.33

readily be calculated. The results of electric calibration of the studied reactions are listed in Table 2.

Verification of the characteristic parameter method

After the thermoanalytical curve of a reaction has been measured, the characteristic thermoanalytical curve data Δ_m, α_m^* and α_T can be obtained, and Φ_m can be calculated from these data and the cooling constant k according to Eq. (6). The kinetic parameter K_n or K_2^* and the rate constant k_n or k_2 can then be calculated according to the mathematical models of the characteristic parameter method. The thermoanalytical curve data and the rate constants of the reactions mentioned above are listed in Tables 3 – 6, in which $k_1^*=k_1$ for a pseudo-first-order reaction. The kinetic parameter of the reaction of formaldehyde with ammonia in aqueous solution is $K_3=144\,k_3\,C_o^2$.

From Tables 3–6, it can be seen that the rate constants of reactions with different orders calculated with this method are in agreement with those to be found in the literature, and the characteristic parameter method is therefore believed to be correct.

Table 4 Thermoanalytical curve data and rate constants for saponification of ethyl propionate at 30°C (solvent: 70% (v/v) EtOH–H_2O)

C_o(ester)/ mol l^{-1}	C_o(KOH)/ mol l^{-1}	Δ_m/ mm	$10^{-4}\cdot\alpha_m^*$/ mm s	$10^{-4}\cdot\alpha_T$/ mm s	R_c	Φ_m	$10^3\cdot k_2$/ l mol^{-1} s^{-1}
0.1067	0.0345	30.5	4.34	5.90	3.09	0.482	1.12
0.06667	0.0125	12.8	2.19	2.87	5.34	0.544	1.35
0.09000	0.0125	16.5	2.34	3.25	7.20	0.471	1.29
0.1133	0.0125	18.2	2.23	3.16	9.06	0.423	1.28
0.1400	0.0125	20.8	2.22	3.21	11.2	0.374	1.31
						Average:	1.29
						Literature value [10]:	1.29

Table 5 Thermoanalytical curve data and rate constants for saponification of ethyl acetate at 30°C (solvent:H_2O; C_o(NaOH)=C_o(ester))

$10^2\cdot C_o$(ester)/ mol l^{-1}	Δ_m/ mm	$10^{-4}\cdot\alpha_m$/ mm s	$10^{-4}\cdot\alpha_T$/ mm s	Φ_m	k_2/ l mol^{-1} s^{-1}
2.00	32.5	4.12	5.20	0.460	0.148
2.50	53.5	6.15	7.56	0.437	0.148
3.00	53.0	5.70	6.80	0.434	0.145
4.00	76.0	7.46	8.65	0.384	0.149
4.50	80.2	7.58	8.97	0.369	0.146
				Average:	0.147
				Literature value [11]:	0.145

Table 6 Thermoanalytical curve data and rate constants for formation of hexamethylenetetramine at 20°C (solvent: H_2O)

C_o(HCHO)/ mol l^{-1}	C_o(NH_3)/ mol l^{-1}	Δ_m/ mm	$10^{-5}\cdot\alpha_m^*$/ mm s	$10^{-5}\cdot\alpha_T$/ mm s	Φ_m	$10^2\cdot k_3$/ l2 mol^{-2} s^{-1}
0.0450	0.0300	28.5	1.31	1.47	0.786	4.93
0.0450	0.0300	29.2	1.34	1.50	0.788	4.91
0.0450	0.0300	31.0	1.40	1.56	0.790	4.98
0.0420	0.0280	22.0	1.22	1.37	0.804	4.38
0.0420	0.0280	24.5	1.26	1.41	0.800	4.80
					Average:	4.80
					Literature value [12]:	4.77*

Determination of the reaction order and the rate constant

The reaction orders and rate constants of the saponifications of ethyl butyrate and the ring-opening reaction of epichlorohydrin with hydrobromic acid were deter-

Table 7 Reaction order and rate constant for saponification of ethyl butyrate at 30°C (thermoanalytical single-curve method)

No.	$[A]_o$/ mol l^{-1}	$[B]_o$/ mol l^{-1}	$10^3\cdot k'$/ s^{-1}	n_a	$-r$	$10^3\cdot\bar{k}$/ s^{-1}
1	0.0600	1.00	2.75	1	0.9999	2.79
2	0.0500	1.00	2.82	1	1.000	
3	0.0400	1.00	2.84	1	0.9999	
4	0.0300	1.00	2.77	1	1.000	
5	0.0200	1.00	2.75	1	0.9999	
1’	0.0500	0.600	1.66	1	1.000	1.68
2’	0.0400	0.600	1.68	1	0.9991	
3’	0.0300	0.600	1.67	1	1.000	
4’	0.0200	0.600	1.65	1	1.000	
5’	0.0100	0.600	1.70	1	0.9997	

	n_a	n_b	n	k_n
Measured value:	1	1	2	$2.79\cdot10^{-3}$ l mol^{-1} s^{-1}
Literature value [13]:	1	1	2	$2.79\cdot10^{-3}$ l mol^{-1} s^{-1}

Solvent: 85% (w/w) $CH_3CH_2OH–H_2O$; $[A]_o$=[KOH]$_o$; $[B]_o$=[ethyl butyrate]$_o$;
r=correlation coefficient

Table 8 Example of thermoanalytical curve analysis (Table 5; No.1)

Δ_i/ mm	$10^{-5}\cdot\alpha_i^*$/ mm s	Φ_i	Δt_i/ s	Fitting formula	$-r$
115.0	1.39	0.543	0	$\ln\frac{1}{\Phi_i}=k't_i$	0.9999
135.0	1.29	0.419	90		
138.5	1.23	0.370	135		
139.8	1.11	0.289	225		
138.0	1.05	0.256	270		
129.0	0.920	0.200	360		
118.0	0.801	0.157	450		
106.0	0.688	0.120	540		
96.8	0.604	0.0945	630		

$\alpha_T = 1.56\cdot10^5$ mm s; k=$2.12\cdot10^{-3}$ s^{-1}; k'=$2.75\cdot10^{-3}$ s^{-1}

Table 9 Reaction order and rate constant for ring-opening reaction of epichlorohydrin with hydrobromic acid at 20°C (thermoanalytical single-curve method)

No.	C_o/ mol l^{-1}	$10^{-5}\cdot\alpha_T$/ mm s	$10^{-5}\cdot\alpha^*_m$/ mm s	Δ_m/ mm	Φ_m	n	$10^2\cdot k_n$ l^2 mol^{-2} s^{-1}
1	0.145	4.79	4.16	90.0	0.743	3	2.18
2	0.150	4.79	4.24	100.5	0.745	3	2.24
3	0.161	4.84	4.22	104.8	0.728	3	2.17
4	0.140	4.29	3.75	80.5	0.749	3	2.28
5	0.120	3.35	3.12	58.0	0.816	3	2.21
					Average:	3	2.16
					Literature value [14]:	3	2.17

Solvent: H_2O

Table 10 Example of thermoanalytical curve analysis (Table 7, No.1)*

$10^{-5}\cdot\alpha^*_i$/ mm s	Δ_i/ mm	Φ_i	Δt_i/ s	n	$10^2\cdot k_n$/ l^2 mol^{-2} s^{-1}
4.68	64.0	0.888	–600	3	2.15
4.56	74.5	0.848	–450	3	2.22
4.42	85.0	0.805	–300	3	2.13
4.29	88.0	0.773	–150	3	2.18
4.03	89.0	0.717	150	3	2.12
3.90	87.5	0.693	300	3	2.15
3.77	84.2	0.670	450	3	2.20
3.64	81.2	0.647	600	2.9	2.29
3.44	74.0	0.615	900	3	2.20
			Average:	3	2.18

* $k=1.50\cdot10^{-3}$ s^{-1}

mined by the thermoanalytical single-curve method, while those of the saponification of ethyl acetate were determined by the thermoanalytical multi-curve method. These results are listed in Tables 7–11.

From Tables 7–11, it can be seen that the reaction orders and rate constants of the above reactions are in good agreement with those in the literature. The thermoanalytical single and multi-curve methods for the determination of reaction orders and rate constants have therefore been validated.

As stated above, the characteristic parameter method can be applied not only to study slow reactions, but also to study faster ones that cannot be studied by the dimensionless parameter method, e.g. the saponification of ethyl acetate, and it can be

Table 11 Reaction order and rate constant for saponification of ethyl acetate at 25°C (thermoanalytical multi-curve method)

$[A]_o$/ mol l^{-1}	$[B]_o$/ mol l^{-1}	Δ_m/ mm	$10^{-4}\cdot\alpha_m^*$/ mm s	$10^{-4}\cdot\alpha_T$/ mm s	Φ_m	$-\log\left(\frac{\Delta_m C_o}{\alpha_T}\right)$	$-\log(\Phi_m C_o)$	$10^2\cdot k_{n_a}$/ s^{-1}	$10^2\cdot k_{n_b}$/ s^{-1}	n_a	n_b	k_2/ l mol^{-1} s^{-1}	r
0.01250	0.1000	57.2	3.56	4.46	0.109	4.795^a	2.866^a						
0.01000	0.1000	43.2	2.69	3.42	0.107	4.899	2.970						
0.00900	0.1000	39.8	2.47	3.11	0.106	4.939	3.020	1.20		1		0.120	0.998
0.00800	0.1000	35.2	2.18	2.65	0.109	4.974	3.059						
0.00600	0.1000	26.8	1.67	2.07	0.111	5.110	3.177						
0.1000	0.01253	52.5	3.29	4.29	0.109	4.814^b	2.865^b						
0.1000	0.01002	43.8	2.74	3.49	0.110	4.900	2.958						
0.1000	0.007158	30.5	1.91	2.51	0.103	5.061	3.112		1.12		1	0.112	0.999
0.1000	0.005727	24.0	1.51	1.93	0.114	5.147	3.185						
0.1000	0.004772	19.2	1.20	1.79	0.0937	5.290	3.358						

Solvent: H_2O; $[A]_o$=[ethyl acetate]$_o$; $[B]_o$=[KOH]$_o$, r=correlation coefficient; $\bar{k}_2$=0.1161 mol^{-1} s^{-1}

a: $C_o=[A]_o$; b: $C_o=[B]_o$

Literature values: [15]: k_2=0.1111 mol^{-1} s^{-1}, n=2;

further applied to determine reaction orders. Thus, the characteristic parameter method broadens the research range of thermokinetics.

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The authors are grateful to the National Natural Science Foundation of China and to the Educational Committee Youth Fund of Sichuan Province for assistance.

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