



Reconstruction of thermodynamic equation of reaction process and its application in DSC/DTA

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ABSTRACT

The traditional thermodynamic equation based on heat flow balance without reflecting the variation characteristics of the reaction process. New thermodynamics equation based on energy conservation is established involving multiple complex factors with reaction process, including species, matter mass and heat capacity. The DSC/DTA equation acquired from energy differential equation. The new equation reflects the dynamic Kirchhoff's law and expresses the heat capacity including the integral term and the differential term which both decided by reaction progression. Two kinds of modes with CaCO_3 reactions are carried out to verify the equation. The theoretical calculations are well in accord with the experimental data, which validates the accuracy and reliability of the new equation.

Reaction process; Thermodynamic equation; DSC/DTA; Thermal capacity

1. Introduction

During the reaction processes, various complicated factors (e.g. variations of species [1,2], mass changes [3,4], internal reaction heat [5]) certainly accompanied these reactions whose reaction heat is closely related to some kinds of thermodynamic parameters in thermodynamic reaction systems, including melting point, decomposition temperature [6], fusing heat [7], crystallization heat [8], and phase change enthalpy [9–13]. The existing thermodynamic theories and thermal analysis techniques e.g. DSC/DTA [14] (Differential Scanning Calorimetry/Differential Thermal Analysis) are used to detect these thermal parameters [15] in studying various reactions, such as glass transition, crystal form transformation, crystal phase change reaction, and metal melting [16,17]. However, DSC/DTA still faces the difficulties to analyze the changing factors in reaction process.

Although DSC and Modulated DSC have been developed for over sixty years, there is still some theoretical problems. For traditional theory, DSC/DTA analysis rely on the theoretical formula basically adopts the approximate relation of total heat flow balance [10,18–20]. The Eqs. (1) and (2) were put forward by Schawe, J. E. K. and M. Reading respectively, mainly applied to the equipment of Mettler Toledo and TA Instruments company. The difference between them is the term of mass.

$$\Phi(T, t) = mc_p\beta + m\Delta h_r \frac{d\alpha}{dt} \quad (1)$$

$$\frac{dQ}{dt} = C_p \cdot \frac{dT}{dt} + f(t, T) \quad (2)$$

Where $\Phi(T, t)$ is the heat flow into the sample, m is the sample mass, β is heating rate of sample, Δh_r is the specific enthalpy of a thermal event (it's actually reaction heat), α is the extent of reaction, Q is amount of heat evolved, C_p is heat capacity, T is absolute temperature, t is time, $f(t, T)$ is some function of time and temperature that governs the kinetic response of any physical or chemical transformation.

The $\Phi(T, t)$ in Eq. (1) and $\frac{dQ}{dt}$ in Eq. (2) follow heat flow balance which is measured in Watts (W), however, conservation of energy should be followed in Joules (J). In other words, the expression of the first law of thermodynamics (energy conservation) is that the total heat is the sum of sensible heat and latent heat. In addition, heat flow is the power at a given time, and the energy should be the change of total energy state in a period of time.

For pure thermophysical process, heat flow balance can directly reflect the differential expression of energy conservation. Nevertheless, it is not applicable for chemical reaction process. The reasons of traditional equations for reaction systems are mainly focus on the following two points.

- (1) The Eqs. (1) and (2) during reaction process do not obey the law of conservation of energy, which essentially replace the law of energy conservation by energy flow/power balance [21], but the experimentally measured heat flows $\Phi(T, t)$ cannot be directly added/or integrated [22]. The total heat flow during reactions is the sum of heat from all thermal physical and thermal chemical reactions, which cannot directly represent the reaction heat ΔE . Especially for a system with multiple coexisting reactions, the measured total sum of heat flows cannot characterize the real energy variations of all elementary reactions in the system [23];

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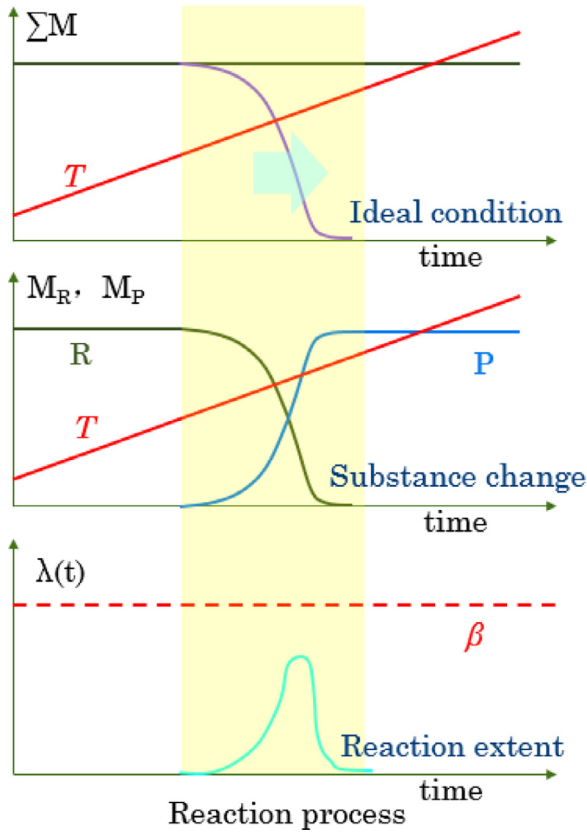


Fig. 1. Diagram of the changes in species and mass of the reaction process.

- (2) The traditional theories ignore the mass m changes and species changes induced by reactions [24], as shown in Fig. 1, the conversion from reactants R to products P is accompanied by a decrease of reacting matter quantity M_R and an increase of produced matter quantity M_P . Moreover, the corresponding heat capacity C_p change accompanying species will lead to an increase of internal energy terms $mC_p\beta$ in the above equation [5], including the internal energy changes of reactants and products rather than a single term. That is, the change of C_p should comply with the Kirchhoff's law [25]: $\Delta_r C_p = \sum \nu C_{p,m}(\text{product}) - \sum \nu C_{p,m}(\text{reactant})$. Furthermore, the reaction conversion rate α belongs to general information, but does not directly correspond to the mass change of any reaction matter. Even in a reaction system with an unchanged total sum of overall reaction mass, the reaction matter masses still decrease and the product masses increase during reactions [26].

Therefore, reaction process should follow the energy conservation equation, and energy flow balance formula, built by differentiate form of energy, is involved in multiple changing factors of reaction process. The vector mathematical expression is introduced to reflect the various changes in the reaction process. The new formula can reflect the physical connotation of the reaction process.

2. Theory

Considering the complicated factors in reaction, the reaction process is assumed to a independent particle model. The species, masses, and heat capacity changing factors of reactions are comprehensively considered. The universal heat flow equation is obtained by differential method, its application equation of DSC/DTA are established by combining test boundary conditions.

2.1. Establishment of thermodynamic equation of reaction system

The thermodynamics systems of reaction processes are considered as independent particle, and the representative physical models of energy are reestablished for a thermodynamic system containing reaction processes. A complete general reaction process (including before-reaction and post-reaction) can be represented as Eq. (3):



where A, B are reactants, C, D are products, a, b, c, d are stoichiometrical coefficients of reactions, ΔE_n is reaction heat, and n is the number of reactions in the system.

As shown in Fig. 2, considering internal heat Q_{in} and external heat Q_{ex} of the reaction system, the equations of energy conservation in the reaction system are established by combining the changes of parameters associated with reactions such as species, masses, heat capacity.

As for the independent particle system, the ideal space-time boundary conditions are assumed as:

- (1) The internal homogeneous state parameters in the reaction system of independent mass points are approximately consistent as expressed by Eq. (4):

$$\frac{\partial[*]}{\partial x_i} \approx 0 \quad [*] \text{ is for } H, T, m \quad (4)$$

Where H is for enthalpy, T is for temperature, m is for mass.

The heating rate $\beta(t)$ could be obtained by Eq. (5) and state parameter temperature T of the reaction system are decided by reaction heat, external heating, and all matters of the reaction system including the unreacted matters. These parameters belong to differential equations of energy conservation, but are not the externally set heating rate, programmed heating rate or other reference values of the reaction system:

$$\beta(t) = \frac{dT}{dt} \quad (5)$$

- (1) All matters in the reaction system at any time point obey the law of mass conservation, and the exchange quantities (in and out of the reaction system) are equal to the mass changing quantity of the system, as expressed by Eq. (6):

$$\sum \dot{m}(\text{system change}) = \sum \dot{m}(\text{boundary exchange}) \quad (6)$$

With all reactants and products are inside the system, that is no overall mass change in the reaction process, the overall exchange is 0 as shown in Eq. (7):

$$\sum \dot{m}(\text{system change}) = \sum \dot{m}(\text{boundary exchange}) = 0 \quad (7)$$

- (1) The specific heat capacities of reactants and products do not vary with temperature, as expressed in Eq. (8):

$$C_{p,i} = \text{const}, \quad i \text{ is for } A, B, C, D \quad (8)$$

Based on the conservation of energy, the thermodynamic equation of the reaction system should be described by Eq. (9):

$$\Delta H = Q_{in} + Q_{ex} \quad (9)$$

For reaction system, ΔH and Q_{in} are expressed by Eqs. (10) and (11),

$$\Delta H = \vec{M}(t) \times \overline{C_p^T} \times T \quad (10)$$

$$Q_{in} = \int_0^t \vec{\lambda}(\tau) d\tau \times \overline{\Delta E^T} \quad (11)$$

The derivative of this formula is given by Eq. (12):

$$\dot{Q}_{ex} = \frac{d\Delta H}{dt} - \dot{Q}_{in} \quad (12)$$

Since matter transformation occurs during the reactions, the physical and mathematical connotations are transformed from one matter

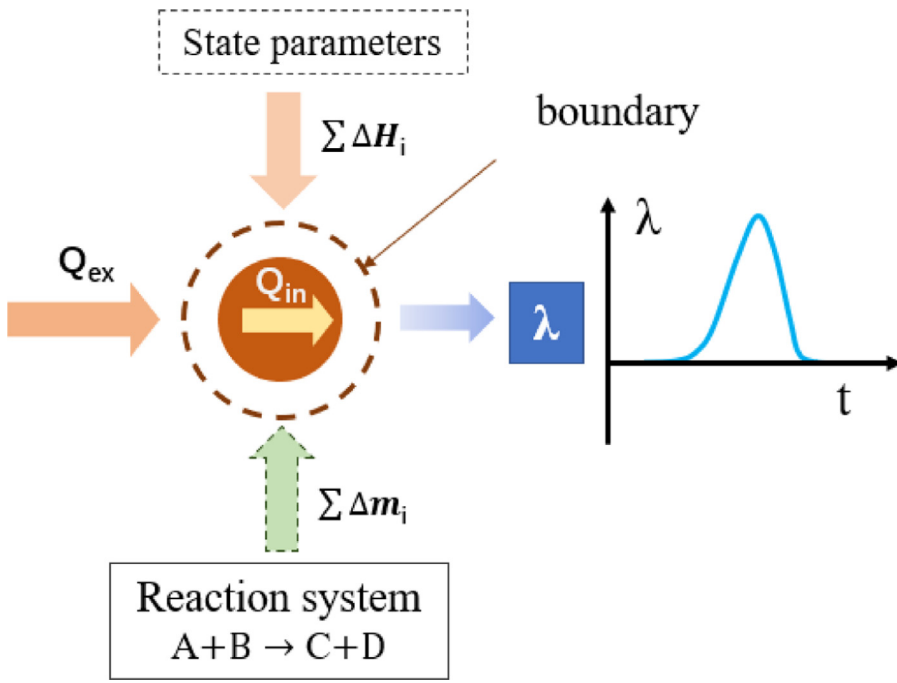


Fig. 2. Diagram of mass and energy variation of a reaction system as an independent particle.

dimension to another matter dimension. For this reason, the thermodynamic equations of the reaction system should be expressed as vectors. The reaction vector composed of multiple reactions is expressed as $\vec{R}$; where the mass variable vector of mass changes from multiple matters is $\vec{M}$; the heat capacity variable matrix of thermodynamic parameters caused by changes of multiple matters is $\vec{C}_p^T$ (transpose of vector of $\vec{C}_p$). As follows in Eqs. (13) and (14):

$$\frac{d\Delta H}{dt} = \vec{M}(t) \times \vec{C}_p^T \times \beta + \frac{d\vec{M}(t)}{dt} \times \vec{C}_p^T \times T \quad (13)$$

$$\dot{Q}_{in} = \vec{\lambda}(t) \times \vec{\Delta E}^T \quad (14)$$

In Eq. (14), $\vec{\Delta E}^T$ is the transpose of vector of reaction heat $\vec{\Delta E}$, $\vec{\lambda}(t)$ is the vector of multiple reaction extent for all reactions.

Thus, the energy conservation equation of complex system with multiple reactions can be obtained as Eq. (15):

$$\dot{Q}_{ex}(t) = \vec{M}(t) \times \vec{C}_p^T \times \beta + \frac{d\vec{M}(t)}{dt} \times \vec{C}_p^T \times T - \vec{\lambda}(t) \times \vec{\Delta E}^T \quad (15)$$

Where, $\vec{M}(t)$ is the variation related to the reaction extent $\vec{\lambda}(t)$ that is expressed by Eqs. (16) and (17):

$$\frac{d\vec{M}(t)}{dt} = \vec{\lambda}(t) \times \vec{R}_W \quad (16)$$

$$\vec{M}(t) = \vec{M}(0) + \int_0^t [\vec{\lambda}(\tau) \cdot \vec{R}_W] d\tau \quad (17)$$

Where, $\vec{R}_W$ is the stoichiometric relation expressed by molecular weight of each reaction, which can be obtained from the Eq. (18):

$$\vec{R}_W = \vec{R} \times \vec{W} = [R_1, R_2, R_3, \dots]^T \times \text{diag}[W_1, W_2, W_3, \dots] \quad (18)$$

Where the $\text{diag}[W_1, W_2, W_3, \dots]$ in Eq. (18) is the form of diagonal matrix.

Substitute the variation of $\vec{M}(t)$ into the energy conservation equation can obtain the Eq. (19):

$$\dot{Q}_{ex}(t) = \vec{M}(0) \times \vec{C}_p^T \times \beta + \left\{ [\vec{\lambda}(t)] \times T + \int_0^t [\vec{\lambda}(\tau)] d\tau \times \beta \right\} \times \vec{R}_W \times \vec{C}_p^T - \vec{\lambda}(t) \times \vec{\Delta E}^T \quad (19)$$

Compared with Eqs. (1) and (2), (19) is based on the law of energy conservation which involves three terms: a reaction initial term $\vec{M}(0) \times \vec{C}_p^T \times \beta$, a reaction drive term $\{[\vec{\lambda}(t)] \times T + \int_0^t [\vec{\lambda}(\tau)] d\tau \times \beta\} \times \vec{R}_W \times \vec{C}_p^T$, and a reaction heat term $\vec{\lambda}(t) \times \vec{\Delta E}^T$. Further, the reaction drive term can be divided into two parts: reaction drive term of temperature $[\vec{\lambda}(t)] \times T \times \vec{R}_W \times \vec{C}_p^T$ and reaction drive term of heating rate $\int_0^t [\vec{\lambda}(\tau)] d\tau \times \beta \times \vec{R}_W \times \vec{C}_p^T$.

Traditional theory replaces the energy conservation law with the simple heat flow balance and ignores the reactants, product types and mass changes that inevitably exist in the reaction process. In Eq. (1) the term $mC_p\beta$ of the traditional equation adopts the system overall mass m and average heat capacity C_p , but ignores the changes in matter masses and types during reactions. In a real reaction process, however, the reaction extent and species must be accurately disassembled. Along with the progression of reactions, the species, mass changes and temperatures in the system all change nonlinearly.

In particular, $\vec{\lambda}(t) \times \vec{R}_W \times \vec{C}_p^T \times T$ can be regarded as a dynamic Kirchhoff law. $\vec{R}_W \times \vec{C}_p^T$ is a vector composed of the standard heat capacities of each reaction. The standard heat capacities of each reaction are the difference between the equivalent heat capacities of all products and reactants in accordance with stoichiometric relations, which represents the essential characteristic parameters of the change of equivalent thermal physical properties of the reaction itself during the transformation of unit substance. As the essential characteristic parameter of different reaction processes, it has nothing to do with the progress of reaction execution and thermodynamic state parameters (such as temperature), and its parameter properties are similar to reaction heat and activation energy.

Eq. (19) is a universal formula which applicable to all kinds of reaction systems. However, for DSC/DTA it should be combined with working mechanism to establish a specific equation.

2.2. Establishment of equation of DSC/DTA

The research object of detection method DSC/DTA is the solid/liquid substance in which physical or chemical reactions taking place in the crucible. Temperature difference between the sample crucible and refer-

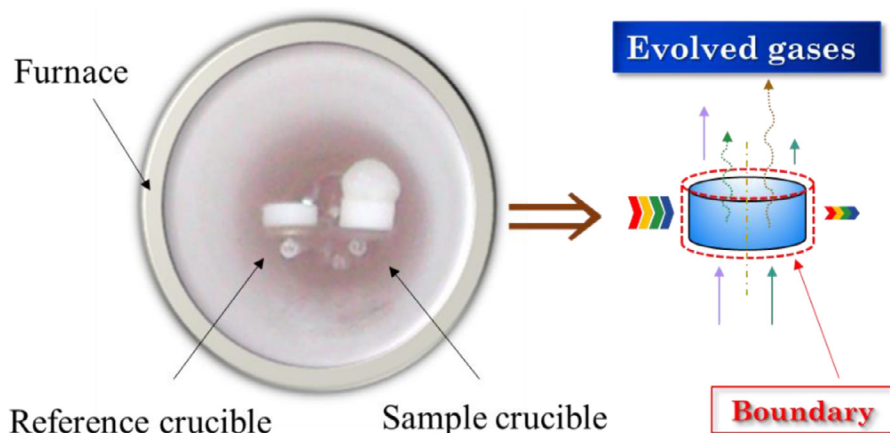


Fig. 3. Model of DSC/DTA detection method.

ence crucible will be caused by reaction heat, and a set of thermocouples placed below the crucible will generate thermoelectric potential. Therefore, DSC/DTA data only represent the solid/liquid phase reaction in the crucible, with no relationship with the heat or secondary reaction of the escaping gases.

DSC/DTA is applicable only to solid and liquid phase energy changes in the reaction system. Clearly, the solid and liquid phase in the reaction system in the crucible are regarded as independent particle system in Fig. 3. The reactions detected by DSC occur in the scale of mass points, and the boundary conditions are the same as the former mass point system. Thus, the expression map relationship of DSC is Eq. (20):

$$\text{DSC/DTA} \Rightarrow [\dot{Q}_{ex}(t)]_{\text{solid/liquid}} \quad (20)$$

The DSC/DTA equation mentioned only represent the solid/liquid phase reaction process in the reaction system. In order to clearly describe the relationship as shown Eq. (21), the DSC/DTA equation does not use the symbol of $[\dot{Q}_{ex}(t)]_{\text{solid/liquid}}$ in Eq. (20).

$$\text{DSC} = \vec{M}(0) \times \vec{C}_p^T \times \beta + \left\{ \left[\vec{\lambda}(t) \right] \times \mathbf{T} + \int_0^t \left[\vec{\lambda}(\tau) \right] d\tau \times \beta \right\} \times \vec{R}_W \times \vec{C}_p^T - \vec{\lambda}(t) \times \vec{\Delta E}^T \quad (21)$$

As same principle of DSC, the heat flow signal detected by DTA differs from DSC by the heat transfer coefficient k , so DTA can be expressed by Eq. (22):

$$\begin{aligned} \text{DTA} &= \frac{1}{k} \cdot \text{DSC} \\ &= \frac{1}{k} \cdot \left\{ \vec{M}(0) \times \vec{C}_p^T \times \beta + \left\{ \left[\vec{\lambda}(t) \right] \times \mathbf{T} + \int_0^t \left[\vec{\lambda}(\tau) \right] d\tau \times \beta \right\} \times \vec{R}_W \times \vec{C}_p^T \right\} - \vec{\lambda}(t) \times \vec{\Delta E}^T \end{aligned} \quad (22)$$

For a single reaction system, $\vec{\lambda}(t)$ can be simplified from vector to scalar as shown in Eq. (23):

$$\text{DTA} = \vec{M}(0) \times \vec{C}_p^T \times \beta + \left\{ \left[\lambda(t) \right] \times \mathbf{T} + \int_0^t \left[\lambda(\tau) \right] d\tau \times \beta \right\} \times \vec{R}_W \times \vec{C}_p^T - \lambda(t) \times \vec{\Delta E}^T \quad (23)$$

Even for reactions whose the overall mass is constant, it means that the sum of the mass of reactants and products keeps constant during all reaction process. Actually the mass of reactants and products respectively varies with the reaction process by themselves. Even if those kinds of reactions, the term of $\left\{ \left[\lambda(t) \right] \times \mathbf{T} + \int_0^t \left[\lambda(\tau) \right] d\tau \times \beta \right\} \times \vec{R}_W \times \vec{C}_p^T$ in Eq. (23) certainly exist during reaction process.

Table 1
Conditions of the thermal analysis experiments.

Samples	Test	Weight (mg)	Heating rate (K/min)	He (mL/min)
CaCO ₃	TG-DTA-MS	20 mg	10	200
CaCO ₃	TG-DTA-MS	20 mg	10 and 20	200
CaCO ₃	TG-DTA-MS	20 mg	Non linear	200

3. Experimental method

To accurately verify Eqs. (21) and (22), CaCO₃ thermal decomposition experiments were studied because these reactions are typical gas-solid reactions with evolved gas and their reaction extension can be determined by the mass product rate of CO₂.

3.1. Materials

The CaCO₃ material with purity of 99.9% was purchased from Aladdin Company.

3.2. Instrumentation

The TG-DTA-MS measurements were performed on the ThermoMass Photo instrument manufactured by Rigaku Corporation [27], which mainly consists of a cylindrical quadrupole mass spectrometry (MS) and a horizontal Thermogravimetry-Differential thermal analyzer (TG-DTA). The ionization of evolved gases is performed using the standard electron ionization (EI) that is 70 eV. Both sample crucible and reference crucible temperatures are measured simultaneously. The temperature of reaction is the temperature of sample instead of crucible and the heating rate is derivative of temperature.

3.3. Experimental scheme

All samples were weighed around 20 mg in Pt crucibles and heated up to 1000 °C with a controlled temperature program. The measurements were carried out at a heating rate of 10 K·min⁻¹ under high purity analytical grade helium dry gas (99.999%) with a flow rate of 200 mL·min⁻¹.

Two types of experiments were chosen as shown in Table 1: I. standard reactions. The solid-phase reactants are decomposed during heating process, with a single product - CO₂ gas. The reaction extent can be determined by using the gas-phase product to prove the consistency of $m(\text{CO}_2)$ and DTG. II Nonlinear temperature program reaction. The universality of the equation is validated with the iteratively modulated heating rate. Multiple variables in Eq. (23) are obtained by temperature-modulated program.

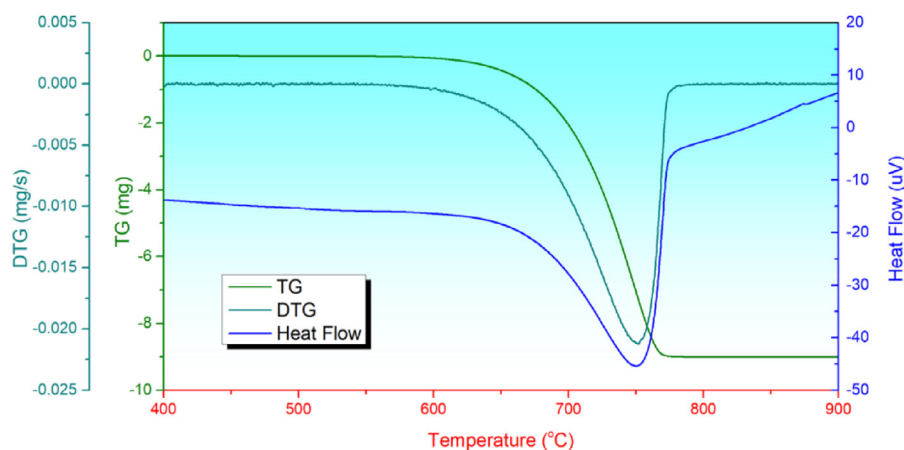


Fig. 4. Schematic diagram of linear heating reaction curves of CaCO_3 .

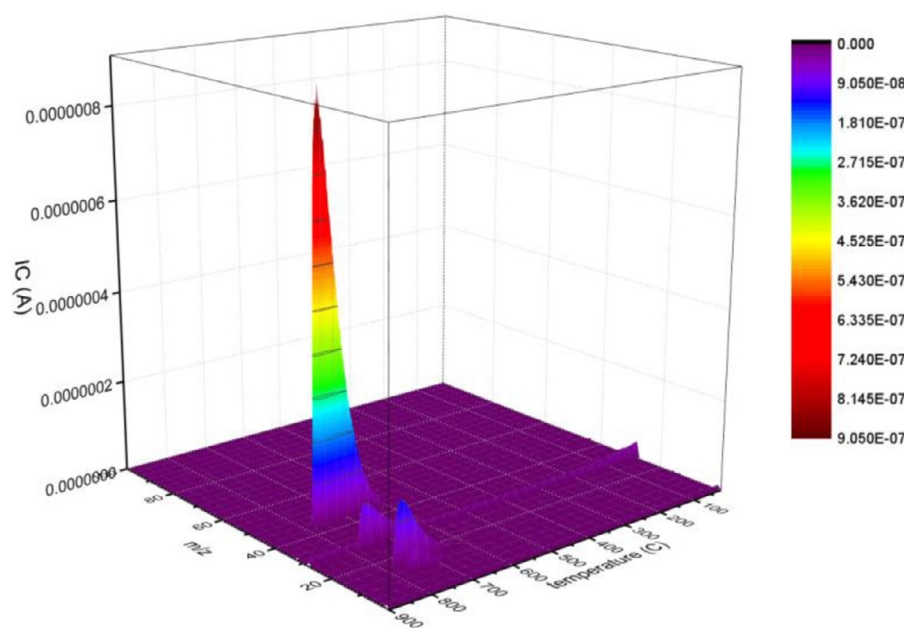


Fig. 5. 3D mass spectrometry of CaCO_3 linear heating reaction products.

4. Results

The mass and energy changing curves of CaCO_3 linear heating reaction are shown in Fig. 4, where the blue curve is the heat flow changing DTA curve during the reactions. Clearly, as the reaction proceeds, the overall mass and energy during reactions both are changing. The TG curve of mass variation, the DTG curve of mass changing rate, and the DTA curve of heat flow change consistently with time.

The product of CaCO_3 decomposition reaction is only CO_2 gas. The ion current intensity changing curve was detected using combined MS. The absolute mass of gases $\dot{m}(\text{CO}_2)$ was measured using MS and analyzed by the quantitative method ECSA [28]. According to stoichiometric relationship of reactions, $\dot{m}(\text{CaCO}_3) - \dot{m}(\text{CaO}) = \dot{m}(\text{CO}_2)$ can be obtained. Then the reaction extent is determined according to gas phase mass flow rate, and the DTG curve of solid phase production rate can mutually validate and obtain accurate reaction real-time extent $\lambda(t)$.

The modulated CaCO_3 heating program was alternated between 10 and 20 K/min, temperature program shown in red, from 550 to 800 °C. The mass and heat flow dynamic changing curves were plotted in Fig. 6, where the yellow curve stands for the DTA curve determined from equations.

The DTG curve illustrates the weight loss rate during CaCO_3 reaction. According to the standard reaction, the DTG curve and $\lambda(t)$ curve

change in a consistent trend, and the changing trend of the TG curve accords with $\int_0^t \dot{\lambda}(\tau) d\tau$. According to the heating rate β during reactions and the curves before and after reactions, the term of thermal capacity change $\overline{C_p}$ can be determined. Thereby, the real-time DTA curve in the reaction system can be interpreted using Eq. (23). As shown in Fig. 6, the simulated yellow curve accords well with the tested blue curve.

The CaCO_3 decomposition reaction is carried out by alternating the different heating rates, and the temperature program is shown in red curve in Fig. 7. During the iterative rising and falling between 550 and 700 °C, the overall temperature program of reactions is equivalent to a constant temperature process, and the mass and heat flow changing curves are shown in Fig. 7. Based on the same method, the real-time DTA curve in the reaction system can be calculated using Eq. (23) and the result accords well with the tested blue curve.

5. Discussion

5.1. Universal applicability of heat flow formula

The heat flow equation Eq. (22) based on the law of energy conservation is applicable to various reactions, including linear heating rate and modulated temperature program. The key concept - reaction extent

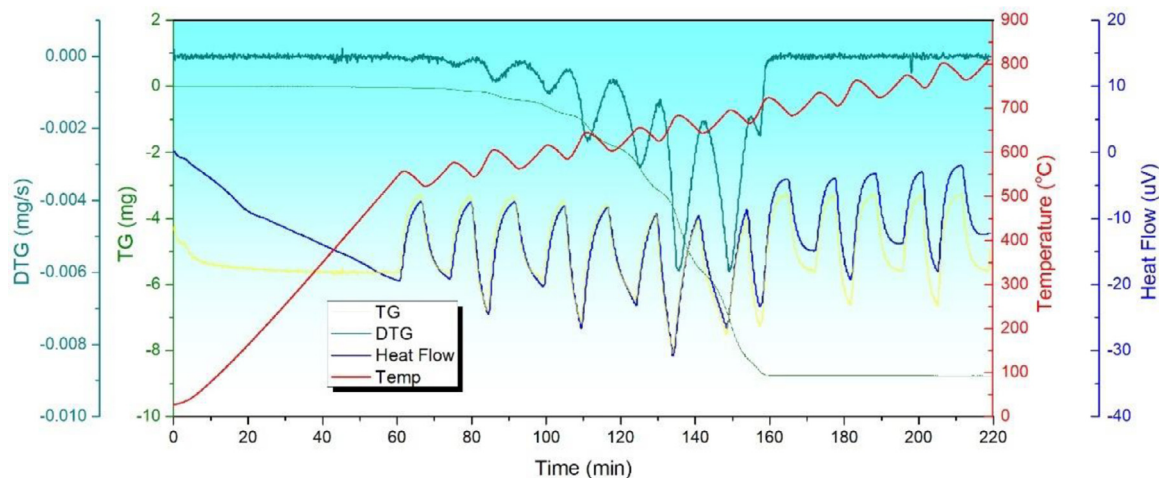


Fig. 6. Decomposition reaction of CaCO_3 with modulated heating – rising in temperature of general trend.

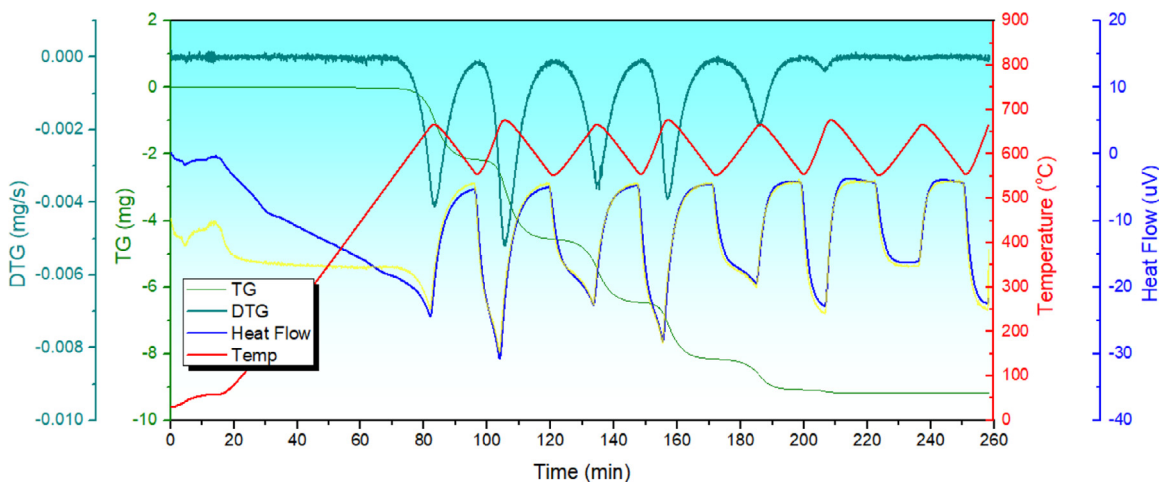


Fig. 7. Decomposition reaction of CaCO_3 with modulated heating - constant temperature of general trend.

Table 2

Comparison of key parameters between Eqs. (23) and (1) or (2).

	Reaction types	mass	Heat capacity
Traditional theory	Not concern	Overall mass	Average C_p or imaginaries
New formula	Disassemble overall reaction	Individual mass $\vec{M}(t)$	Dynamic Kirchhoff's law $\{[\lambda(t)] \times T + \int_0^t [\lambda(\tau)] d\tau \times \beta\} \times \overline{R_W} \times \overline{C_p^T}$

$\lambda(t)$ in the equation decides various changing factors in the reactions, such as species change, mass change, and heat absorption or release during reactions. Compared with the traditional theory, the Eq. (23) is different in the following points: it is based on the law of energy conservation, it adopts the differential form of energy equation to derive the heat flow equation; it adopts vectors that apply to multi-reaction and multi-matter systems; it considers the various parameters induced by reactions, including matter change, mass change, and heat capacity change as shown in Table 2.

As for reactions with gas release, the absolute masses of released gases can be used to calculate the reaction extent and thereby to solve the thermodynamic parameters of the reaction process. The heat flow expression in Eq. (23) indicates it is universally applicable in the whole-time extent.

Further simplify the Eq. (23) in stages of reaction, before the reaction starts, the formula can be reduced to Eq. (24):

$$DSC(t < t_{onset}) = \vec{M}(0) \times \overline{C_p^T} \times \beta \quad (24)$$

After the reaction, the formula can be reduced to Eq. (25):

$$DSC(t > t_{end}) = \vec{M}(0) \times \overline{C_p^T} \times \beta + \int_0^t [\lambda(\tau)] d\tau \times \beta \times \overline{R_W} \times \overline{C_p^T} \quad (25)$$

In the reaction process, Eq. (23) is related to the system temperature, temperature rising rate, and reaction progression. The heat flow in the process is not constant, and the masses of reactants r and product p are changing with time, and the sample temperature is also changing with time. The term of heat capacity change involves the interaction between two changing parameters.

5.2. Theoretical limit of the traditional method

The heat flow balance in Eqs. (1) and (2) does not conform to the law of energy conservation, which is limited by severe loss of physical meaning. The heat flow entering a sample, $\Phi(T, t)$, is described as two components i.e. sensible heat flow and latent heat flow and directly adds the two together: $\Phi(T, t) = mc_p\beta + m\Delta h_r \frac{da}{dt}$. However, the reaction process must obey the law of energy conservation, and heat flow is a

Table 3

Comparison of different theoretical interpretations of heat capacity variations.

C_p	Schawe J. E. K's theory	Reading M.'s theory	New formula
Term of T	$C's(T, w)$	$C_p \cdot b$	$[\vec{\lambda}(t)] \times T \cdot C_p$
Term of β	$j C''s(T, w)$	$C_p \cdot \cos(\omega t)$	$\int_0^t [\vec{\lambda}(\tau)] d\tau \times \beta \cdot C_p$

differential term of energy against time: heat flow DSC= dQ/dt . Since the masses of reactants and product (m_R , m_P), and temperature T are dynamically changing at the same time, heat flow will physically and mathematically show several differential terms different from the equation.

5.3. The reason for the existence of complex parameters of heat capacity

When Eqs. (1) and (2) are adopted to analyze the heat capacity term in the modulated DSC curves, different scholars offered various explanations such as thermal relaxation due to thermal hysteresis is employed. Consequently, the specific heat capacity C_p of the sample becomes frequency dependent. Thereby, a compound equation is used to describe the specific heat function of the reaction process, and a compound term containing a real part and an imaginary part is introduced in Table 3.

According to Eq. (23), the primary cause for heat capacity change is the difference of reaction heat capacity, namely $\{[\vec{\lambda}(t)] \times T + \int_0^t [\vec{\lambda}(\tau)] d\tau \times \beta\} \times \overline{R_W} \times \overline{C_p}^T$ in the equation, where $\int_0^t [\vec{\lambda}(\tau)] d\tau \times \beta$ and $[\vec{\lambda}(t)] \times T$ correspond to the imaginary part and real part of the traditional equation, respectively. Also, based on the Reading M's theory, the terms $\int_0^t [\vec{\lambda}(\tau)] d\tau \times \beta$ and $[\vec{\lambda}(t)] \times T$ correspond to the reversible and irreversible part that only for heat capacity of substance.

Both terms are associated with the reaction progression and are characteristic parameters of the reaction but are unrelated to the specific heat capacity of matters. Meanwhile, this term can also be comprehended as the reaction driven term of heat flow. Namely, it exists along with the progression of reactions, and it is zero before or after reactions.

6. Conclusions

A thermodynamic equation involving the reaction progression is established in accordance with the law of energy conservation, and the accurate expressions of many dynamic parameters in the reaction system (e.g. mass change, species change, system specific heat capacity change) during thermodynamic reactions are presented. As for the heat capacity change during reactions, the equation involves a heat capacity change term decided by the reaction progression and elaborates the relationship between two types of expressions in the change terms. This equation is universally feasible to various reaction systems. Together with commercial equipment's testing principles, the solid/liquid-phase reaction system in the crucible is regarded as independent mass points, and the DSC/DTA equation and the connotation of its baseline are presented.

Declaration of Competing Interest

The authors declared that they have no conflicts of interest to this work.

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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