

TEMPERATURE MODULATED DSC Theoretical interpretation

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Abstract

The application of non-linear heating program to a heat-flux DSC apparatus has attracted much attention. From thermodynamics viewpoint, it is shown that the variation of enthalpy of a sample changing with temperature change is due, to both the true heat capacity of the sample and the enthalpy of some transformations occurring in the sample, characterized by its degree of advance. Using the simple assumption that the rate of the transformation is proportional to the distance from the thermodynamic equilibrium, an electrical model of the thermal event is given. Using the coupled cell model of the DSC apparatus, we show how to obtain the rate of transformation of the sample and heat capacity, which is directly related to the base line of the experiment.

Keywords: base line, DSC, kinetics, modeling, thermodynamics, TMDSC

Introduction

Since the original Boersma [1] DSC, the development of data acquisition systems has made significant improvements of their performances and a better understanding of the material properties. In DSC experiments, the temperature is the physical variable, and the system responds with a thermodynamic change toward its equilibrium at the programmed temperature. The rate of change is kinetically controlled by experimental conditions.

The step-wise non-linear heating rate method were used in 1970's [2–5]. In fact, this method is time consuming, and not widely used. It is however helpful to distinguish fast and slow transformations [6, 7].

The use of a sine modulation superposed to a linear heating rate was described by Birge and Nagel [8, 9] in AC calorimetry, and they interpreted their results as a frequency dependent heat capacity. The similar modulation was used in a DSC apparatus [10–15]. This technique has led to a large number of papers [16–17], but even in the most recent

papers, the interpretation of the data is not yet firmly established. Several papers were dealing with the modeling of the instrument itself [18, 19].

The interpretation of the results based on the description given by Birge and Nagel [9]. They represent the heat capacity of the sample C_p as a complex heat capacity [20–25]:

$$C_p = C + jC^* \quad (\text{with } j^2 = -1),$$

where C is the real heat capacity and C^* is the imaginary part. The real heat capacity is called ‘the reversible heat capacity’ and the imaginary part is called ‘the irreversible heat capacity’. The irreversible heat capacity is generally associated with the advance of some transformation occurring in the sample, including a reversible transformation. In fact, the physical meaning of the complex heat capacity is unclear [26–28].

It is reasonable to ask if a new definition of heat capacity has to be used, or if a new interpretation based on thermodynamics, as shown by Schawe [29] should be developed.

This paper is based on a thermodynamic and kinetic description of the systems [30]. No distinction is attempted between physical and/or chemical transformations, such as phase transitions or reversible reactions. The purpose of this paper is to establish a model of a transformation, usable with the accepted model of disc-type heat-flux DSC [31–39]. The calorimetric signal can be computed, or from the calorimetric signal, the thermodynamic and kinetic data of the transformation can be computed.

Kinetics, thermodynamics and DSC

DSC is at the junction of three sciences:

- thermodynamics describes the equilibrium state of the system under the experimental conditions,
- kinetics gives the rate at which the system changes towards equilibrium,
- heat transfer describes the instrument used for the study of the system.

An examination of DSC should take these facts into account.

Thermodynamics

It was shown by Prigogine [30] that the most general thermodynamic description of a system requires at least three variables. Enthalpy of the system is given by $H(T, P, \xi)$, ξ being the degree of advance of some transformation occurring in the system. DSC experiments are usually done at a constant pressure.

For a simple equilibrium, where A and B make an ideal solution



The equilibrium constant is given by:

$$K_{\text{eq}} = \frac{x_B}{x_A} = \exp\left(-\frac{\Delta_r G_T^\circ}{RT}\right) = \frac{\xi_{\text{eq}}}{1-\xi_{\text{eq}}} \quad (2)$$

where x_B and x_A are the molar fraction of B and A respectively.

Of course, $\Delta_r G_T^\circ = \Delta_r H_T^\circ - T\Delta_r S_T^\circ$ where $\Delta_r H_T^\circ$ is the enthalpy change of the transformation and $\Delta_r S_T^\circ$ is its entropy change at temperature T .

Apparent heat capacity C_p of the system is given by:

$$C_p = \frac{dH}{dT} = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} + \left(\frac{\partial H}{\partial \xi}\right)_{p,T} \frac{d\xi}{dT} \quad (3)$$

and $C_{p,\xi} = \left(\frac{\partial H}{\partial T}\right)_{p,\xi}$ is its true heat capacity [30]. The enthalpy change of the reaction is

$$\Delta_r H_T^p = \left(\frac{\partial H}{\partial \xi}\right)_{p,T} \quad \text{and} \quad \Delta_r H_T^p \frac{d\xi}{dT}$$

is its conformational heat capacity [30]. On differentiating the equilibrium constant (2) with respect to the temperature it follows [30]:

$$\frac{d\xi_{\text{eq}}}{dT} = \frac{\Delta_r H_T^\circ}{RT^2} \frac{K_{\text{eq}}}{(1+K_{\text{eq}})^2} \quad (4)$$

Kinetics

In a conventional DSC, the temperature is a linear function of time, and (3) can be written as the enthalpy time derivative:

$$\frac{dH}{dt} = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} \frac{dT}{dt} + \left(\frac{\partial H}{\partial \xi}\right)_{p,T} \frac{d\xi}{dt} \quad (5)$$

It is obvious that the heat flux ϕ required to warm the system at a heating rate β , is the sum of the heat flow absorbed by the heating of the sample ($C_{p,\xi}$) and that absorbed by the transformation. This last relationship is rewritten as:

$$\phi = \beta C_{p,\xi} + \Delta_r H_T^p \frac{d\xi}{dt} \quad (6)$$

From the above equation the experimental difference between apparent and true heat capacity relies on the kinetics of the transformation.

Assuming that the transformation given in (1) is near equilibrium, its rate is given by:

$$\frac{d\xi}{dt} = k_1(1-\xi) - k_2\xi \quad (7)$$

with $k_i = A_i \exp(-E_i/RT)$, where A_i and E_i are respectively the preexponential factor and the enthalpy of activation of (2) in the direction $i=1$ or $i=2$.

At equilibrium $d\xi/dt=0$. On identification in (7), it follows:

$$\Delta_r H_T^\circ = E_1 - E_2 \quad \text{and} \quad \Delta_r S_T^\circ = R \ln \frac{A_1}{A_2} \quad (8)$$

At time $t=0$, the degree of advance of the transformation is ξ and the equilibrium value is ξ_{eq} . The distance to equilibrium $\Delta\xi$ is written

$$\Delta\xi = \xi - \xi_{\text{eq}} \quad (9)$$

Since temperature is a function of time, on differentiating with respect to time:

$$\frac{d\Delta\xi}{dt} = \frac{d\xi}{dt} - \left(\frac{d\xi_{\text{eq}}}{dT} \right) \frac{dT}{dt} \quad (10)$$

And upon substitution:

$$\frac{d\Delta\xi}{dt} = (k_1 + k_2)\Delta\xi + \frac{\Delta_r H_T^\circ}{RT^2} \frac{K_{\text{eq}}}{(1+K_{\text{eq}})^2} \frac{dT}{dt} \quad (11)$$

Study of transformation, in a system submitted to a non-linear heating rate

The purpose of this study is to lay out the equations leading to an electrical modeling of a transformation, usable with an electrical model of a DSC apparatus.

A very simple and crude description of the rate of transformation is used. From equation (7), it is assumed that the rate is simply proportional to the distance to equilibrium:

$$\frac{d\xi}{dt} = -k(T)\Delta\xi \quad (12)$$

Furthermore, it is assumed that $k(T)$ does not change significantly in a small temperature range.

Sinusoidal modulation of the temperature around a constant temperature

The temperature $T(t)$ of the sample is given by

$$T(t) = T_f(t) + A \sin(\omega t) \quad \text{with} \quad T_f(t) = T_0 \quad (13)$$

where the parameters have the following meaning: T_0 : constant temperature, A : amplitude of the modulation, f : frequency (Hz) $\omega = 2\pi f$

The amplitude of the temperature modulation is assumed to be small, as compared to the range of temperature of the transformation. It is possible to linearize the change of the degree of advance of the transformation at equilibrium with temperature $T(t)$ as given in Eq. (12):

$$\begin{cases} T(t) = T_0 + A \sin(\omega t) \\ \xi_{\text{eq}} = \xi_{\text{eq}}(T_0) + \left(\frac{d\xi_{\text{eq}}}{dT} \right)_{T=T_0} A \sin(\omega t) \end{cases} \quad (14)$$

Equation (12) can be rewritten as:

$$\frac{d\xi}{dt} = -k(T) \left(\xi - \xi_{\text{eq}}(T_0) + \left(\frac{d\xi_{\text{eq}}}{dT} \right)_{T=T_0} A \sin(\omega t) \right) \quad (15)$$

This equation can be solved with the assumption that non-linear effects due to the modulation of the kinetic coefficient k by the temperature oscillations can be neglected:

$$\xi = \xi_{\text{eq}}(T_0) + \frac{k^2(T_0)}{\omega^2 + k^2(T_0)} \left(\frac{d\xi_{\text{eq}}}{dT} \right)_{T=T_0} A \sin(\omega t) - \frac{\omega k(T_p)}{\omega^2 + k^2(T_0)} \left(\frac{d\xi_{\text{eq}}}{dT} \right)_{T=T_0} A \cos(\omega t) \quad (16)$$

Finally the heat flux as computed in Eq. (6) is

$$\begin{aligned} \frac{\varphi(t)}{A} = & \left(C_{p\xi} + \frac{k^2(T_0) \Delta_r H_T^\circ}{\omega^2 + k^2(T_0)} \left(\frac{d\xi_{\text{eq}}}{dT} \right)_{T=T_0} \right) \omega \cos(\omega t) + \\ & + \frac{\omega^2 k(T_0) \Delta_r H_T^\circ}{\omega^2 + k^2(T_0)} \left(\frac{d\xi_{\text{eq}}}{dT} \right)_{T=T_0} \sin(\omega t) \end{aligned} \quad (17)$$

Sinusoidal modulation of the temperature plus a constant heating rate β

The temperature $T(t)$ of the sample is given by (12) with:

$$T_f(t) = T_0 + \beta t \quad (18)$$

The degree of advance is decomposed into two parts: one linked to the linear heating rate called the filtered degree of advance $\xi_f(t)$ and the other, to the modulated part of the temperature $\delta\xi(t)$. It follows

$$\xi(t) = \xi_f(t) + \delta\xi(t)$$

Due to the linearity in ξ , Eq. (12) giving the rate of the transformation is then broken into two separate equations:

$$\left\{ \begin{array}{l} \frac{d\xi_f}{dt} = -k(T_f)(\xi_f(t) - \xi_{eq} T_f(t)) \\ \frac{d[\delta\xi(t)]}{dt} = -k(T_f) \left(\delta\xi - \xi_{eq} T_f - \left(\frac{d\xi_{eq}}{dT} \right)_{T=T_0} A \sin(\omega t) \right) \end{array} \right. \quad (19)$$

The second equation of (19) giving $\delta\xi(t)$ is similar to the Eq. (15), with the filtered temperature T_f instead of the constant temperature T_0 . The fluctuating part of the degree of advance behaves as if it were alone in the vicinity of T_f , and its analysis can be done accordingly.

Electrical representation of a system with a transformation

Equations (6), (12) and (14) are written with complex notations:

$$\left\{ \begin{array}{l} \varphi(t) = j\omega C_{p\xi} T + j\omega \Delta H_T^P \xi \\ j\omega \xi = -k(T)(\xi - \xi_{eq}) \\ \xi_{eq} = T \left[\frac{d\xi_{eq}(T)}{dT} \right]_{T=T_f} \end{array} \right. \quad (20)$$

which gives

$$\xi = \frac{k}{k + j\omega} \left[\frac{d\xi_{eq}}{dT} \right]_{T=T_f} T$$

Upon substitution, it follows:

$$\varphi = \left(j\omega C_{p\xi} + \frac{j k \Delta_r H_T^P}{k + j\omega} \left[\frac{d\xi_{eq}}{dT} \right]_{T=T_f} \right) T$$

or

$$\varphi = \left[\frac{\omega^2 k \Delta_r H_T^P}{k^2 + \omega^2} \left[\frac{d\xi_{eq}}{dT} \right]_{T=T_f} + j\omega \left(C_{p\xi} + \frac{k^2 \Delta_r H_T^P}{k^2 + \omega^2} \left[\frac{d\xi_{eq}}{dT} \right]_{T=T_f} \right) \right] T \quad (21)$$

The heat flux is decomposed into a flux (real part) in-phase with the temperature of the furnace, and into an out-of-phase heat flux (imaginary part). The electrical analogy of this transformation is represented by an impedance Z made of a resistor ρ in parallel with a capacitor C . With

$$\frac{1}{Z} = \frac{1}{\rho} + jC\omega \tag{22}$$

The theoretical expression of ρ and C are:

$$\rho = \frac{1}{\omega^2 k \Delta_r H_T^P \left[\frac{d\xi_{eq}}{dT} \right]_{T=T_f}} \tag{23}$$

$$C = C_{p\xi} + \frac{k^2 \Delta_r H_T^P}{k^2 + \omega^2} \left[\frac{d\xi_{eq}}{dT} \right]_{T=T_f} \tag{24}$$

Much more simple relations can be obtained by substitution of ρ in (22).

$$C - C_{p\xi} = \frac{k}{\rho \omega^2} \tag{25}$$

and

$$\frac{1}{Z} = \left[\frac{1}{\rho} + j\omega \left(C_{p\xi} + \frac{k}{\omega^2 \rho} \right) \right] \tag{26}$$

Discussion

Equation (21) and followings give a simple description of a transformation in a sample. It is represented by a capacitor with a resistor in parallel. The capacitor has the usual meaning of a true heat capacity, and the resistor represents the part of the heat flux exchanged between the sample and the outside caused by the progress of the transformation. Depending on the kinetics of the transformation, several cases are studied.

True heat capacity

When the enthalpy of the system under study is a function of two state variables $H=f(T,P)$ such as sapphire below its melting temperature, it follows that $\Delta_r H_T^o = 0$. Then from (23) ρ is infinity and the thermal impedance Z reduces to:

$$Z = \frac{1}{j\omega C_{p\xi}} \tag{27}$$

Case $\omega \ll k$

The rate of transformation is large. From (22), the impedance Z of the system is:

$$\frac{1}{Z} = j\omega \left(C_{p\xi} + \Delta H_T^p \left[\frac{d\xi_{eq}}{dT} \right]_{T=T_f} \right) \quad (28)$$

Measurement of Z gives the apparent heat capacity designed as C_p , and it is not possible to get the true heat capacity.

Case $\omega \gg k$

The impedance Z of the system is written as:

$$\frac{1}{Z} = \left[k\Delta H_T^p \left[\frac{d\xi_{eq}}{dT} \right]_{T=T_f} + j\omega C_{p\xi} \right] \quad (29)$$

It is divided into a real part and an imaginary one. The real part contains the rate of the transformation and the imaginary one contains the true heat capacity.

Case $\omega \sim k$

In fact, at low temperature $k \ll \omega$ then $C_p = C_{p\xi}$ and at higher temperature $k \gg \omega$ as discussed above. The impedance of the system change from (28) to (29).

The apparent heat capacity of the system C given by (24) shows an increase for a higher frequency.

Thermal effect without equilibrium

The transformation is controlled by kinetics only, i.e. the system is a function of two state variables or in other words the enthalpy change vanishes. Hence Eq. (27) is valid, only a heat capacity is seen.

Physical meaning

The physical meaning of the heat capacity $C_{p\xi}$ is clear. The resistor ρ is the electrical representation of the path followed by the heat flux leaving or entering the sample during the transformation. If the transformation is endothermic, then $\rho > 0$, and $\rho < 0$ in the opposite case.

Complex DSC model

A widely accepted model [31–39] of a disc-type heat flux DSC apparatus is given in Fig. 1. On the product side, the impedance Z is given in (22). The heat capacity C is the sum of the heat capacities of the crucible, the thermoelectric disc and the true heat capacity of the sample. On the reference side, C' is the sum of the heat capacities of the reference material plus the crucible and the disc.

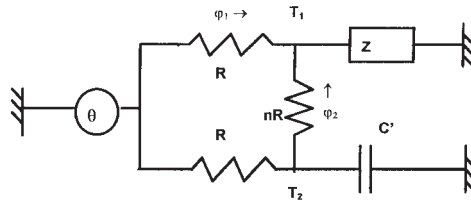


Fig. 1 Representation of a heat flow DSC apparatus: θ =temperature of the furnace; T_1 =temperature of the product; T_2 =temperature of the reference; R =furnace-crucible resistor; nR =crucible-crucible resistor; C' =reference side capacitor; Z =product side impedance; ϕ_1 =heat flux furnace-sample; ϕ_2 =heat flux furnace-reference

Of course, only the modulated part of the signals are concerned (furnace, reference and sample temperatures). Equations giving the heat flux on the reference and product side respectively, are combined with the equations relating the temperatures and the calorimetric signal ΔT are given in (30).

$$\left\{ \begin{array}{l} \phi_1 = \frac{\theta - T_1}{R} \\ \phi_2 = -\frac{\Delta T}{nR} \\ \Delta T = T_1 - T_2 \\ j\omega C'(T_1 - \Delta T) = \frac{\theta + \Delta T - T_1}{R} - \phi_2 \\ T_1 = Z(\phi_1 - \phi_2) \end{array} \right. \quad (30)$$

The solution of these equations gives the complex impedance Z of the transformation.

$$Z = -R \frac{[(1+n)\Delta T + n\theta + jnRC'\omega\Delta T]}{\Delta T(2+n) + jRC'\omega[\Delta T + n(\Delta T - \theta)]} \quad (31)$$

Upon identification of the complex and real parts of Z with (22), C and ρ are obtained. From (23) and (24) $C_{p\bar{\xi}}$ and k can be computed, as discussed in chapter Discussion.

Conclusions

The theoretical analysis of a heat flux DSC apparatus, used with a linear plus a sine modulation of the temperature of the furnace, allows for the determination of the true heat capacity of a sample, even during a time and temperature dependent thermal effect.

The filtered signal, give the apparent heat capacity. The difference between the apparent and the true heat capacity is the thermal power developed by the transformation in the sample. By integration, with respect to time the enthalpy change is computed.

The base line of a DSC experiment is defined [38] as 'the calorimetric signal obtained if no thermal event occurs in the sample'. The knowledge of the true heat capacity of the sample gives a way to establish the base line. We conclude that the puzzling problem of the base line in DSC may have a rigorous solution, giving more results than an intuitive approach.

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