Journal of Thermal Analysis, Vol. 9 (1976 405—414

TOPOLOGICAL ASPECTS OF DIFFERENTIAL THERMAL ANALYSIS

G. DRĂGAN

Institute of Chemical Research,
ICECHIM, Spl. Independentei 202, Bucharest, Romania

(Received October 15, 1975)

The most important calorimetric methods have been reviewed: the differential thermal analysis (DTA) as basic disposition and the scanning calorimetry (DSC) as well as the adiabatic rate calorimetry (ARC). The thermal circuits of these are expressed by bond diagrams as conceived by topological thermodynamics. It has been stated that the heat flux associated with the process of transformation is virtually (uncompensated) transferred in the DTA system, really transferred (compensated) in the DSC and ARC systems, between the two containers through a transfer medium assumed to be purely dissipative.

Calorimetry was developed along with the notions of thermodynamics. Thus, drop calorimetry is the most direct means for studying the state functions (enthalpy, entropy, encraty etc.) through the response measurable C_p or C_v [1]. Until recently, the time evolution of these functions was not taken into account. The main factors were considered to be the close heat leakage between the source (generator) and the sample, and the lower amplitude of the thermal perturbation (adiabatic transfer), and additionally the usage of a low performance system of measurement and control of the adiabatic conditions. Therefore, the perturbing flux is assumed to be transferred to the material instantaneously and isotropically.

Following the extension of these calorimetry studies, it was noticed that the measurables show specific peculiarities around a critical temperature with certain materials. In these domains, the equilibrium thermodynamics are no longer valid, as for $T \rightarrow T_c$ the equilibrium of the system is ever harder to attain, even under isothermal conditions, because of the critical fluctuations [2]. Thus, however low the perturbation may be, it can no longer be considered as being transferred under adiabatic conditions. Recent studies [3] on a large number of organic substances defined as glassy crystals have demonstrated that in an adiabatic calorimetric system the state functions are subjected to relaxation phenomena associated with certain processes of structural changes. The influence of the characteristics of the thermal perturbation on the response of the material could be emphasized for these cases. Lately, the process of transformation denoted as T_m^1, also observed in polyethylene through the response measurable $C_p(T)$ by flash calorimetry [4], could be thoroughly studied [5].

In general, it can be stated for all transformation phenomena that a perturbation of the system induces phenomena of mass and energy transfer into the material. In this case we shall have to resort to non-equilibrium thermodynamics for the interpretation of the response measurables. The scanning calorimetric methods recently developed, such as differential thermal analysis (DTA) [6], differential scanning calorimetry (DSC) [7, 8] and adiabatic rate calorimetry (ARC) [9], allow more rapid revelation of these transformations. The scanning technique is based on the indirect (the case of the DTA system) or direct (the case of DSC and ARC systems) recording of the heat fluxes exchanged between the source and the material during the calorimetric round. This operation is effected through a measurable function of the whole system. The purpose of the present work is to find a way of developing a formalism of interpretation of a heat flux associated with the process of transformation, keeping in mind the phenomena of transport occurring in the calorimetric round. Two general common aspects will be taken into account *viz.* the relaxation nature of the heat and mass transfer process, and the composite nature of the material subjected to the process of transformation. These two aspects justify the approach of the non-equilibrium thermodynamics in the topologic concept recently devised by Oster and Auslander [10] for the case referring to the establishment of external thermal circuits of the three calorimetric systems taken into account.

Constitutive relations

The DTA system is the simplest one, lying at the basis of the other two mentioned above. Figure 1 shows this *basic disposition* [7], that can be represented after the following description:

Equipotential surfaces C (the surface of the generator), C_R (the surface of the reference container) and C_S (the surface of the sample container) have at the moment t the temperatures T, T_R and T_S, respectively. Between C and C_R, on the one hand, and C and C_S, on the other, the respective exchanged fluxes $w_1(t)$ and $w_2(t)$ are transferred through the medium R, assumed to be purely dissipative [10].

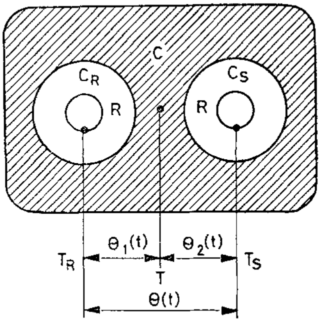

Fig. 1. Schematic representation of the DTA system as basic disposition

The two circuits are assumed to be independent. These natural fluxes can be expressed by the gradients $\Theta_1 = T - T_R$ and $\Theta_2 = T - T_S$, respectively, taking into account the finite propagation speed of the thermal perturbation [11], through the relationship:

$$w_i(t) = \int_0^t M(t - t')\,\Theta_i(t')\,dt', \qquad i = 1, 2. \tag{1}$$

This convolution relation can be abbreviated as follows:

$$w_i(t) = M \otimes \Theta_i, \qquad i = 1, 2 \tag{1'}$$

or

$$\tilde{W}_i(p) = \tilde{M}(p)\,\tilde{\Theta}_i(p), \qquad i = 1, 2 \tag{1''}$$

where the upper sign defines the Laplace transformation and p is the complex variable [12]. The function $M(t)$ is defined in the theory of heat transfer with finite speed, as the *heat-flux relaxation function* [11], and is characteristic of the leakage medium R.

In the DTA system the response measurable is the differential signal $\Theta = \Theta_1 - \Theta_2$. As in all measurement systems, this is assumed to be linear. Physically, this can be expressed as follows: if a process of transformation associated with an internal heat flux $w(t)$ is produced in a container (for instance C_S), then the causality condition [13] can be written as follows:

$$\Theta(t) = \int_0^t R(t - t')\,w(t')\,\mathrm{d}t' = R \otimes w \tag{2}$$

or

$$\tilde{\Theta} = \tilde{R}\tilde{W} \tag{2'}$$

From the general theory of linear systems (see e.g. [12]), the function $\tilde{M}(p)$ is defined as the *transfer function*, and $\tilde{R}(p)$ as the *response function* of the system, the relationship

$$\tilde{M}(p) = 1/\tilde{R}(p) \tag{3}$$

existing between them.

By subtraction of Eq. (1) we get

$$\tilde{W} \equiv \tilde{W}_1 - \tilde{W}_2 = \tilde{M}\tilde{\Theta} \tag{4}$$

which can also be obtained through a reversal of Eq. (2), taking into account (3). This result formally expresses the fact that the flux $w(t)$ of the transformation process is virtually transferred between the two containers C_S and C_R through the purely dissipative medium characterized by the transfer function $1/\tilde{R}(p)$.

Equation (2) represents the response $\Theta(t)$ of the system at the moment t, if the perturbation flux starts at the moment $t' = 0$. In order to evaluate the total amount of energy E of the transformation process, the flux is considered to extend over the time interval ($t_{\text{initial}} = 0$, $t_{\text{final}} = T$), so that

$$E = \int_0^T w(t)\mathrm{d}t.$$

For a unitary step function as perturbation, defined as

$$w^1(t') = \begin{cases} 0, & \text{for } t' < 0 \\ 1, & \text{for } t' \geq 0 \end{cases}$$

the corresponding response will be

$$\Theta^1(t) = \int_0^t R(t')\mathrm{d}t', \quad \text{or} \quad \tilde{\Theta}^1(p) = \tilde{R}/p. \tag{5}$$

Taking into account the equality (5), we can rewrite Eq. (2) as

$$\tilde{\Theta} = \tilde{R}\tilde{W} = p\tilde{\Theta}^1\tilde{W} \tag{6}$$

or

$$\tilde{\Theta}/p = \tilde{\Theta}^1\tilde{W}$$

which becomes

$$\int_0^t \Theta(\tau)\mathrm{d}\tau = \Theta^1 \otimes w = \int_0^t \Theta^1(t - t')\, w(t')\mathrm{d}t' \tag{6'}$$

through inverse transformation [12]. It can be considered that the integral $\int_0^t R(t')\mathrm{d}t'$ for $t \to \infty$ exists and is finite, so that

$$R = \int_0^\infty R(t')\mathrm{d}t'$$

defines the *equilibrium thermal conductivity* of the leakage medium [11]. Then, for integration on the domain of existence of the process $w(t)$ Eq. (6′) becomes

$$E = \int_0^T w(\tau)d\tau = \frac{1}{R}\int_0^T \Theta(\tau)\mathrm{d}\tau, \tag{6''}$$

which represents precisely the relationship used to estimate the amount of energy in the DTA system [6].

The fluxes $w_i(t)$ are considered as being accumulated by the containers C_R and C_S, respectively. The constitutive relation for this process of purely capacitive accumulation [10] can be written as

$$C_{R,S}\frac{\mathrm{d}T_{R,S}}{\mathrm{d}t} = w_{1,2}(t) \tag{7}$$

Bond diagrams for the thermal circuits

Starting from the constitutive relations formulated above, one can represent the thermal circuits for the cases of the three types of scanning calorimeters. The concept of bond diagram given by Oster and Auslander for an energetic circuit in general will be used. Together with the description of circuits in these terms, the basic elements of this concept will be reviewed.

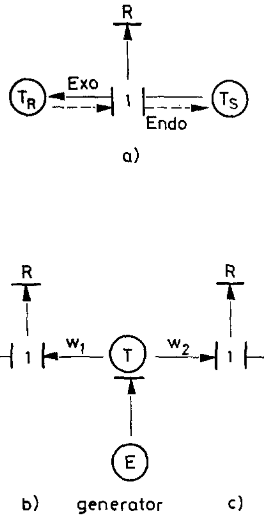

Fig. 2. Bond diagrams of the DTA thermal circuits

The DTA system as basic disposition is essentially expressed by Eq. (4) of the virtual transfer of the flux $w(t)$ between the two containers through the medium R. The bond diagram corresponding to this virtual circuit is represented in Fig. 2a.

The flux $w(t)$ is the same in the branches of the 1-junction, according to Kirchhoff's law for currents [10] in purely dissipative elements. This diagram results from summing up the diagrams in Figs 2b and 2c, which describe the independent circuits of the two containers. In these diagrams, the causality of the branches for equal current junctions (1-junctions) and equal temperatures (0-junctions) [10], has been expressed in the concept of Oster and Auslander.

The differential equation associated for instance with the circuit of the container C_R, can be written by taking into account the constitutive relation of the purely dissipative element, the Ohm equation (4), and the purely capacitive equation (7). Equation (4) becomes successively:

$$C_R p \tilde{T}_R = \tilde{W}_1 \tag{4'}$$

for taking into account (1″)

$$\tilde{T}_R = \frac{1}{(1 - pC_R\tilde{R})}\tilde{T}. \tag{8}$$

If the generator is considered to provide the equipotential surface at the temperature $T(t) = Kt$, then $\tilde{T}(p) = K/p^2$ [12], and Eq. (8) becomes

$$\tilde{T}_R = \frac{K}{p^2(1 - pC_R\tilde{R})}. \tag{8'}$$

The product $C_R\tilde{R} \equiv \tau_R$ is the time constant for the capacitive accumulation of the element C_R through the dissipative medium R, while through transformation, Eq. (8) yields the solution (see ref. [12], Annexed Table)

$$T_R(t) = Kt + K\tau_R(e^{-t/\tau_R} - 1). \tag{9}$$

The result obtained is similar to that obtained by Kessis [6], taking into account a coefficient of superficial transfer between the two surfaces. By subtraction of the analogous equation obtained for the sample circuit in Eq. (9), the evolution of the baseline in the absence of the internal flux $w(t)$ results:

$$\Theta_0(t) = K(\tau_K e^{-t/\tau_R} - \tau_S e^{-t/\tau_S}) + K(\tau_S - \tau_R). \tag{10}$$

After a period of relaxation $\tau > \tau_{R,S}$, the baseline becomes horizontal and is shifted to zero with $K(\tau_S - \tau_R)$ [6]. Under these conditions it is necessary that $T(t) = Kt$ and not any other function should be programmed through the generator [6]. If, on the other hand, we eliminate the capacitive elements from the circuits ($\tau_{R,S} \to 0$), the baseline remains unmodified through the equilibration $w_1 \simeq w_2 \approx 0$, the flux $w(t)$ alone subsisting. This elimination is effected precisely

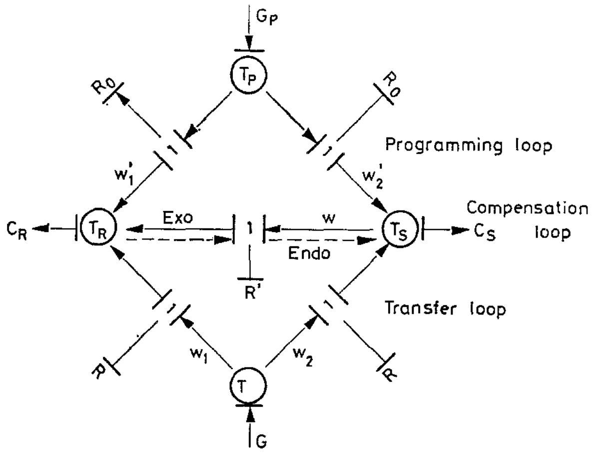

Fig. 3. Bond diagram of the DSC thermal circuits

through the extrapolation of the baseline to the $w(t)$ effect, through the tangent method. If this retardation effect is negligible, the condition $T(t) = Kt$ is no longer compulsory, because a boundary condition has not been necessary to estimate the total amount of energy E through (6″), as the temporary limiting of the effect is sufficient. For the isothermal case, the diagram in Fig. 2a shows the very case of the Tian–Calvet type conduction calorimetry for which the relation analogous to (2′) and (6″), as well as the explicit form of the function $R(t)$, have been established [14].

The DSC system [7, 8] has a compensation circuit of the flux $w(t)$, thus maintaining the temperature of the container C_S at the same value as that of C_R.

Figure 3 gives the bond diagram of the three thermal circuits, namely: (i) the transfer loop through the dissipative medium R, left from the basic disposition; (ii) the programming loop through generator G_p, by means of which T_R and T_S are maintained at an established evolution in time; and (iii) the compensation circuit by means of which a flux $-w(t)$ is superposed between the two containers through an artificial transfer function $1/R'$. If the two dissipative media R_0 and R are naturally achieved, the medium R' results as a combination between these. Hence, for the case of attaining the steady-state response ($t > \tau_{R\,S}$) [8], the following relationships can be written

$$\tilde{W}_1 = \frac{1}{\tilde{R}}(\tilde{T}_R - \tilde{T}), \qquad \tilde{W}_2 = \frac{1}{\tilde{R}}(\tilde{T}_S - \tilde{T}) \tag{11}$$

$$\tilde{W}_1' = \frac{1}{\tilde{R}_0}(\tilde{T}_R - \tilde{T}_P), \qquad \tilde{W}_2' = \frac{1}{\tilde{R}_0}(\tilde{T}_S - \tilde{T}_P) \tag{12}$$

$$\tilde{W} = \frac{1}{\tilde{R}'}(\tilde{T}_R - \tilde{T}_S) \tag{13}$$

corresponding to the three circuits. Applying the conservation law between the values

$$\Delta\tilde{W} = \tilde{W}_1 - \tilde{W}_2 = \frac{1}{\tilde{R}}(\tilde{T}_R - \tilde{T}_S)$$

$$\Delta\tilde{W}' = \tilde{W}_1' - \tilde{W}_2' = \frac{1}{\tilde{R}_0}(\tilde{T}_R - \tilde{T}_S)$$

we can write

$$\tilde{W} = \Delta\tilde{W} + \Delta\tilde{W}' = \left(\frac{1}{\tilde{R}} + \frac{1}{\tilde{R}_0}\right)(\tilde{T}_R - \tilde{T}_S)\,. \tag{14}$$

Comparing this result to Eq. (13), we obtain

$$\frac{1}{\tilde{R}'} = \frac{\tilde{R}_0 + \tilde{R}}{\tilde{R}\tilde{R}_0} \tag{15}$$

which is an identical result to that obtained by O'Neill (ref. [8], Eq. 2). Equation (15) shows that the compensation flux $w(t)$ directly measured in the DSC system is really transferred (by the compensation loop) between the two containers through a dissipative medium with transfer function $1/R'$.

The ARC calorimetric system [9] records the flux $w(t)$ associated with the transformation process, as also in the case of the DSC system.

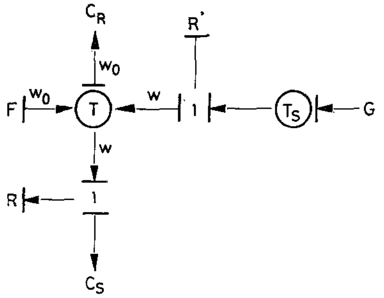

Fig. 4. Bond diagram of the ARC thermal circuit

Figure 4 shows the bond diagram for the programming circuit (here denoted by the constant flux element F) [10] and the compensation circuit found within this system. The constant flux generator programmes the sample container C_R (without any sample material) to a linear increase or decrease of temperature. In the presence of the sample, part of the flux w_0 is accumulated by this. In order to maintain the sample programming, the flux $w(t)$ is compensated. From the diagram it follows that $R = R'$. In this case of the ARC system, the flux $w(t)$ is really transferred between the container and the sample through the leakage medium.

References

1. H. E. Stanley, Introduction to Phase Transitions and Critical Phenomena, Clarendon Press, Oxford, 1971, ch. I.
2. K. Kawasaki, Ann. Phys., 61 (1970) 1.
3. O. Haida, T. Matsuo, H. Suga and S. Seki, Proc. Japan Acad., 48 (1972) 489.
4. Gh. Drăgan, Lucr. Conf. Nat. Chim. Anal. 3rd, 4 (1971) 351; Materiale Plastice, 10 (1973) 87.
5. Gh. Drăgan, Rev. Roumaine Chim., 20 (1975) 687.
6. J. J. Kessis, Compt. Rend. Acad. Sci. Paris, 270 (1970) 1, 120, 265.
7. E. Bonjour, M. Couach, R. Lagnier and J. Pierre, B. I. S. T. Commissariat à l'Energie Atomique, 180 (1973) 7.
8. M. J. O'Neill, Anal. Chem., 36 (1964) 1238.
9. M. J. Buckingham and C. Edwards, Rev. Sci. Instrum., 44 (1973) 1167.
10. G. F. Oster and D. M. Auslander, J. Franklin Inst., 292 (1971) 1.
11. M. E. Gurtin and A. C. Pipkin, Arch. Rational Mech. Anal., 31 (1968) 113.

12. G. Doetsch, Anleitung zum praktischen Gebrauch der Laplace-Transformation und der Z-Transformation, München, 1967.
13. R. Kubo, J. Phys. Soc. Japan, 12 (1957) 570.
14. M. Hatori, S. Tanaka and K. Amaya, Bull. Chem. Soc. Japan, 43 (1970) 1027.

Résumé — Mise au point sur les méthodes calorimétriques les plus importantes: l'analyse thermique différentielle (ATD) comme technique de base, l'analyse calorimétrique différentielle à compensation de puissance (DSC) et la calorimétrie à vitesse adiabatique (ARC). Les circuits thermiques de ces techniques s'expriment par des diagrammes de liaisons comme ceux conçus par la thermodynamique topologique. On établit que le flux de chaleur associé au processus de la transformation est virtuellement transferré (sans compensation) en ATD et réellement transferré (avec compensation) en DSC et ARC, entre les deux conteneurs par un milieu de transfert supposé être purement dissipatif.

Zusammenfassung — Eine Übersicht über die wichtigsten kalorimetrischen Methoden, sowie die Differentialthermoanalyse (DTA) als Grundverfahren, die Abtastkalorimetrie (DSC) und die adiabatische Geschwindigkeitskalorimetrie (ARC) wird gegeben. Die thermischen Kreise derselben werden durch Bindungsdiagramme, wie sie an Hand der topologischen Thermodynamik erhalten werden, ausgedrückt. Es wurde festgestellt, dass die Wärmeströmung mit dem Umwandlungsprozess assoziiert scheinbar (unkompensiert) in das DTA-System, wahrhaftig (kompensiert) in die Systeme DSC und ARC übertragen wird, undzwar zwischen den zwei Behältern durch ein als rein zerstreuend angenommenes Transfermedium.

Резюме — Представлено обозрение наиболее важных калориметрических методов: дифференциальный термический анализ (ДТА) в качестве основного метода, дифференциальная сканирующая калориметрия (ДСК) и адиабатическая скоростная калориметрия (АСК). Термические циклы их выражены с помощью диаграмм связи, построенных на основе топологической термодинамики. Установлено, что тепловой поток, связанный с процессом превращения, фактически не компенсированным переносился в системе ДТА и компенсированным переносился в системе ДСК и АСК. Установлено также, что перенос его между двумя приемниками через массообменную среду должен быть чисто рассеянным.