

A Critique on the Analysis of DSC and DTA Curves

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Two approaches for the analysis of DSC and DTA curves have been examined experimentally using pure indium and anthracene as well as by electric and infrared pulse heating of the sample container. Melting curves of triangular shape were obtained. The approach based on the theory of heat transfer was found to be valid in the melting of pure substances. On the other hand, the other approach based on the linear theory of control and measurement was found to be valid in the electric heating and the infrared irradiation experiments by examining linearity and superposition. The differing results depending on conditions are explained by the fundamental equation of heat transfer and apparatus design.

INTRODUCTION

Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are broadly applied techniques for the determination of the thermal properties of organic and inorganic materials. Two contradictory approaches for analysing DSC and DTA curves have been proposed. One is the usual method used in purity determination by DSC, and the other is based upon the linear theory of control and measurement by assuming a superposition principle.

In the purity determination by DSC, reduction of DSC curves to real melting curves is made by correcting the recorded temperature using the slope of a triangular DSC melting curve of an ultra pure substance such as indium.¹⁾ The theoretical basis of this temperature correction was given in O'Neill's paper.²⁾ The triangular shape of a DSC melting curve of an ultra pure material is due to heat transfer, and the slope equals the heat transfer coefficient. A similar triangular DTA melting curve was also given in a paper by Smyth.³⁾ It was calculated by the finite difference method assuming an infinite plate. Another similar triangular melting curve was also observed by DTA.⁴⁾ From these facts, some similarity between DSC and DTA is vaguely suggested.

On the other hand, applying the linear theory of control, Tateno⁵⁾ proposed a method of DTA curve reduction to real curves of reaction rate. The reduction was done by deconvolution using a transfer function obtained by evolving heat with a resistance heater in the sample container. He analysed a DTA curve of the

decomposition of calcium oxalate kinetically. Recently, a method based on the same theory has also been proposed by Tachoire.⁶⁾ In his proposed method he used an analog electronic circuit of the inverse transfer function to reduce curves of temperature change observed with a conduction calorimeter as well as with a differential calorimetric analysis* apparatus to real curves of heat evolution or consumption due to the reaction under investigation. The reduction can be made on line in real time. A paper, similar to Tachoire's work but mathematical in approach, has been presented by Tanaka.⁷⁾ He employed frequency transfer function which can be obtained from the response to stepwise heat evolution precisely. He stated that his method was both of general and easy applicability and of high precision. In all of the above papers, linearity is assumed. The linear theory of control and measurement was also applied to the analysis of DSC curves of polyethylene melting.⁸⁾

In order to elucidate validity or limitation of these contradictory approaches, fundamental responses of DSC and DTA apparatus to pulse heat evolution or consumption, idealized hypothetically in these theories, should be examined experimentally.

As stated above, temperature correction of the DSC purity determination is carried out using the triangular melting curve of an ultra pure material. In the theory, sample weight should not influence the slope of the triangular response. Similar triangles of the same slope

* This term (used in the original paper of Tachoire) has been rejected by the ICTA Committee on Nomenclature. The present author uses it to transfer exactly the meaning which Tachoire intended to express.

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and of a height proportional to the square root of the sample weight should be obtained by changing the sample weight. These responses are shown schematically in Fig. 1. Contrarily, in the linear theory of control and measurement, the linearity or additivity of the superposition principle is assumed. Thus, the height of the response to different magnitudes of pulse heat evolution or consumption of equal duration should be proportional to the power, schematically shown in Fig. 2. When triangular curves are obtained, the slope is proportional to the power or the sample weight. Additivity should also hold upon successive heat evolutions or consumptions. The response to pulse heat evolution can be synthesized by adding successive responses to two successive pulses of half duration. Obviously, these two conclusions are incongruent and can be resolved only by critical experiments.

In this report, the author evaluated the two approaches by experimental examination of the fundamental assumptions of both approaches. The melting of pure substances and heat evolution with an electric

heater are utilized as a pulse phenomena, see Figs. 1 and 2. Data from other workers were also examined. Either approach has been found to be valid in a limited area, *i.e.*, triangular curves are obtained for melting of pure substances, while linearity holds in the case of heat evolution with the electric heater. The reason for this contrast can be understood by examining the fundamental equations of heat transfer.

EXPERIMENTAL

Sample -- Indium (99.999% purity) foil (0.1 mm thick) was purchased from Furu-uchi Chemicals Co., Ltd., and circular specimens of the same diameter as the sample pans were cut out of the foil. The specimens and the sample pans were cleaned ultrasonically in distilled benzene and dried. The anthracene used was zone-refined.

Apparatus -- The DSC used was manufactured by Rigaku Denki Co., Ltd. (No. 8055). To improve the precision of temperature measurement, a reverse bias

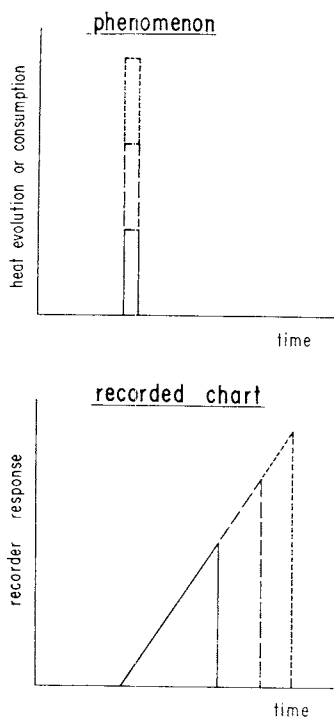


Fig. 1. Schematic drawings of the dependence of response on the amount of pulse heat evolution or consumption, according to the theory of heat transfer. The solid, long dashed and short dashed lines in the two graphs correspond to the same process.

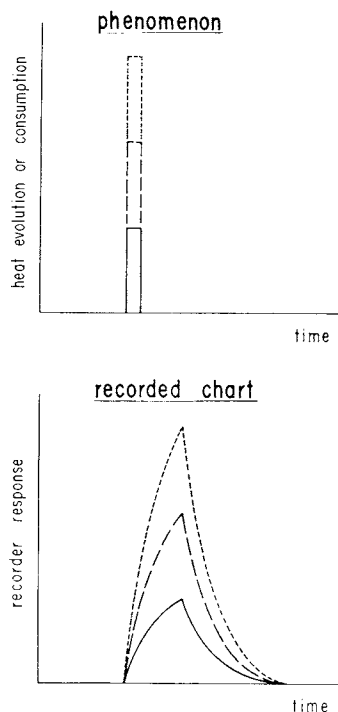


Fig. 2. Schematic drawings of the dependence of response on the amount of pulse heat evolution or consumption, according to the linear theory of control and measurement. The solid, long dashed and short dashed lines in the two graphs are as in Figure 1.

voltage is fed against the temperature output signal from a DC voltage standard (Yokokawa Electric Works, Ltd., type 2853). The full scale, 2 mV, covers the 25 cm chart width. The micro-sample DTA used for observation of melting was constructed by the author and is reported elsewhere.⁹⁾

RESULTS AND DISCUSSION

First, melting curves of the pure indium and anthracene were obtained by DSC. The dependence of the curves on the sample weight is shown in Figs. 3 and 4.

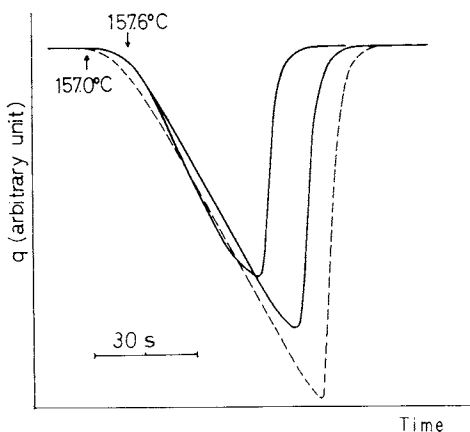


Fig. 3. Typical DSC curves of melting of different amounts of pure indium. The curves are superposed on the same temperature scale. The dashed line curve was obtained on heating the melted sample again.

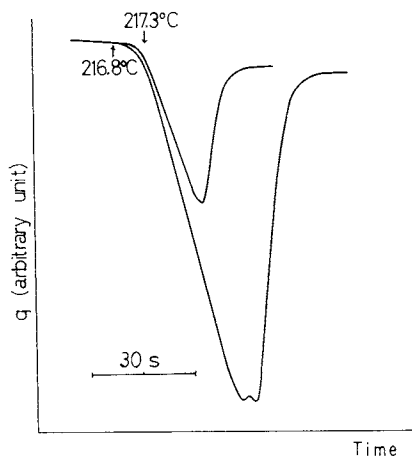


Fig. 4. Typical DSC curves of melting of different amounts of pure anthracene. The curves are superposed on the same temperature scale.

These curves were all obtained at a heating rate of 2.5 K min^{-1} in the ambient atmosphere. As is clearly seen in the figures, almost triangular melting curves were observed. The slope and the height are listed in Table 1. It is evident from these data that the slope, which corresponds to the heat transfer coefficient of O'Neill's theory, is almost the same in all cases and is independent of the sample weight. The height is roughly proportional to the square root of the sample weight. Takahama and Ichihara also observed that the slope is independent of the heating rate with a Perkin-Elmer DSC apparatus (type 1B).¹⁰⁾

Table 1. Dependence of Slope and Height of Triangular Melting Curves on Sample Weight, w .

Indium			
Sample Weight w/mg	Slope*	Peak Height*	
6.5	14.2	10.0	
10.3	13.4	12.7	
15.6	15.2	17.8	
24.8	15.2	21.8	
35.2	15.6	27.2	
Anthracene			
Sample Weight w/mg	Slope*	Peak Height*	
1.0	10.3	6.3	
1.9	12.6	11.8	
2.8	12.3	13.7	
6.5	15.9	25.8	

* The dimensions of the slope and the peak height are common for the indium and the anthracene and are in arbitrary units.

Experimental evidence indicates that the linear theory of control and measurement can not be applied to DSC curves of the melting of pure substances, but the theory based on heat transfer holds. Moreover, the slope of the indium melt does not differ essentially from that of anthracene. This suggests that heat transfer outside the sample effects the slope.

Similar triangular melting curves are obtained with the micro-sample DTA apparatus at a heating rate of 800 K h^{-1} in the ambient atmosphere, see Fig. 5 where some typical curves for the anthracene are reproduced. Similar results were also obtained using pure indium. The slope is almost independent of the sample weight, and the height is roughly proportional to the sample weight and not proportional to its square root. This may be due to long tailing on the DTA curves. In the theory of O'Neill, heat content is neglected. However the heat content of the sample, its container and materials surrounding them can not be neglected

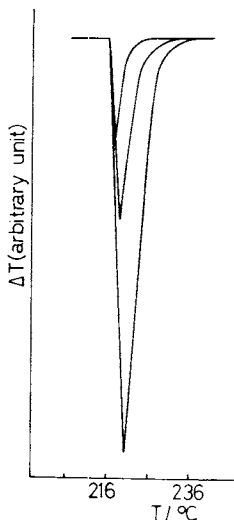


Fig. 5. Typical DTA curves of melting of different amounts of pure anthracene. The curves are superposed on the same temperature scale.

especially in a DTA apparatus. The long tailing is due to this heat content. In spite of this oversimplification, the theory of O'Neill seems to be roughly applicable to DTA curves of the melting of pure substances. The linear theory of control and measurement is not valid for the DTA curves.

The above-mentioned similarity between DSC and DTA should now be discussed. In usual DSC apparatuses, the arrangement of an inner heater, a temperature-sensor and a sample container is as shown in Fig. 6. The temperature or the heating rate is controlled by negative feedback from the sensor to the heater. Thus, it is not the sample but the sensor that is controlled and heated at a constant rate. The heat flowing into the sample depends on the temperature gradient between the sample and the adjacent sensor (Fig. 6(a)) or between the sample and the adjacent heater (Fig. 6(b)) whose temperature is also increased linearly to maintain a constant heating rate (constant temperature gradient between the sensor and the heater). The heat transfer depends on the gradient.

At steady state where no transition nor reaction occurs, the heat-flow to the sample is constant and there are constant temperature gradients between the sample, the heater and the sensor. When a transition or reaction occurs, the heat-flow to the sample becomes increased or decreased due to the change of temperature gradients between the sample and the other components. Because of the above mechanism of heat transfer, the sample is not heated up at the constant rate, but the

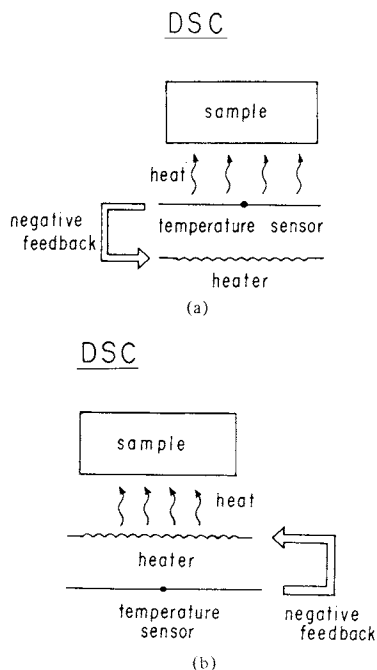


Fig. 6. Schematic drawings of heater, temperature-sensor and sample arrangement in a DSC apparatus.

heating rate of the sample changes during the transition or the reaction, while the sensor is heated up at the constant rate. Thus, the definition of DSC is realized only partly; the heat-flow to the sample is measured, but the heating rate of the sample is not maintained at a constant rate. The mechanism of the heat-flow is quite similar in DTA where the metal block is heated up at a constant rate, and heat, proportional to the temperature gradient between the sample and the metal block, flows into the sample, see Fig. 7. Because of this mechanism of heat transfer, the temperature difference between the sample and the reference material in DTA is proportional to the difference in the heat-flow between them. In DSC the inner heater plays the role of

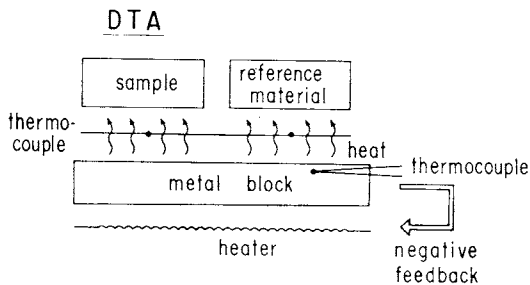


Fig. 7. Schematic drawings of the arrangement of a DTA apparatus.

the DTA metal block, and the difference in the heat-flow itself between the sample and the reference material is measured directly instead of the temperature difference as in DTA. Because the heat flows by the same mechanism in DSC and DTA and either the difference in the heat-flow or the temperature difference proportional to it is recorded in either apparatus, the recorded curves become similar to each other.

However, there are some differences between DSC and DTA. For instance, the thermal mass around the sample is larger generally in DTA than in DSC, and the heat transfer coefficient is smaller in DTA than in DSC. Because of these differences, thermal response time is larger generally in DTA than in DSC. Thus, tailing after the transition or the reaction becomes longer in DTA than in DSC.¹¹⁾

From the above considerations, we can conclude that DSC curves are the same in nature as DTA curves, but the large tailing on the DTA curve prohibits the reduction of the curves to a real curve of heat evolution or consumption in most cases. It is also inferred that the theory based on heat transfer^{1,2)} can be applied to the DSC curves of pure substances.

However, there is other evidence which supports the linear theory of control and measurement. The curves reproduced in Fig. 8 were obtained with an electric heater placed within the sample container in a quantitative DTA apparatus (for calibration of the apparatus). These results were reported elsewhere.¹²⁾ The duration of the heat evolution is the same, but the power is

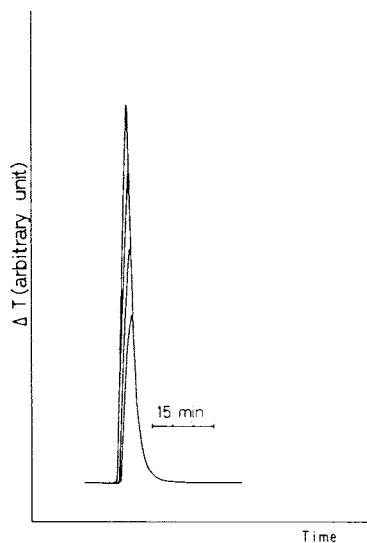


Fig. 8. DTA curves obtained by electrically heating the sample container of a quantitative DTA apparatus maintained at 350°C for 160 seconds.

different in these curves. The height of the peak is proportional to the power, *i.e.*, the linearity holds.

Conclusive evidence is shown in Fig. 9. These curves were also obtained during calibration of a commercial model of the same quantitative DTA apparatus.¹³⁾ The peak height is also proportional to the power. In another way, the superposition principle is proved to hold by using these curves, as is shown in Fig. 10. Here, a DTA curve of 120 seconds duration is synthesized by adding successively two DTA curves of 60 seconds heat evolution of the same power, shown as thin lines in the figure. The synthesized curve is identical to the recorded curve of a 120 seconds heat evolution. Similarly, a DTA curve of 240 seconds heat evolution can be synthesized by adding successively the two DTA curves of 120

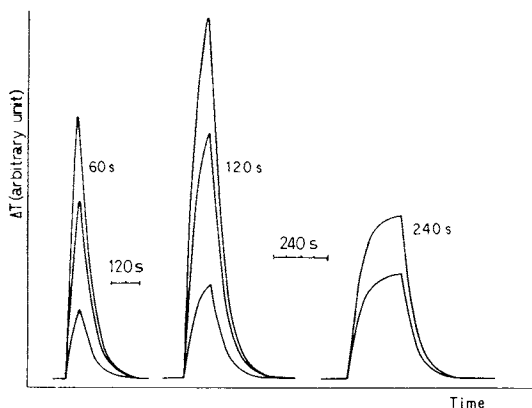


Fig. 9. DTA curves obtained by electrically heating the sample container of a quantitative DTA apparatus maintained at 450°C. The curves of the same duration are superposed on each other. The duration of three series is indicated in the figure.

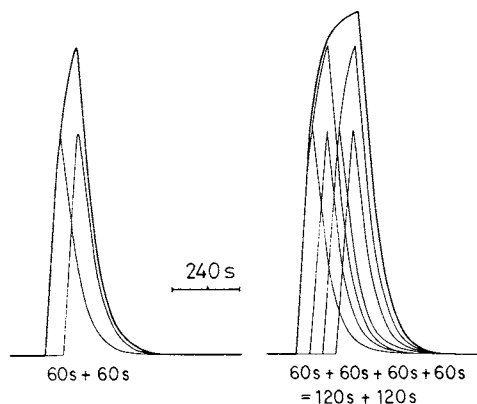


Fig. 10. DTA curves synthesized by successive superposition of DTA curves of electrical heating of short duration (shown as thin lines). The duration is indicated in the figure.

seconds heat evolution at the same power or the four DTA curves of 60 seconds heat evolution at the same power, shown in Fig. 10. The synthesized curve is the same as the recorded one. Thus, the linear theory of measurement and the additivity or the superposition principle hold in the curve of the electric evolution of heat within the DTA sample container.

Because of the similarity between DSC and DTA, the superposition principle is expected to hold in DSC. Indeed, Flynn¹⁴⁾ has obtained experimental evidence which supports the superposition principle. He observed the response of a DSC to pulsed infrared radiation on the sample pan and reported the response to irradiation of differing duration. As is shown in Fig. 11, the synthesized curves obtained in the same way are quite the same as the recorded ones.

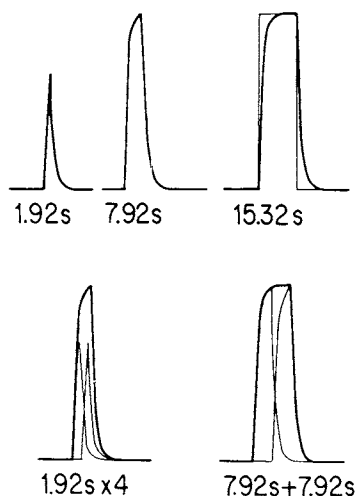


Fig. 11. DSC curves obtained on infrared irradiation of the sample cell for indicated times by Flynn (top), and DSC curves synthesized by successive superposition of DSC curves of infrared irradiation of indicated short durations (bottom). The thin line in the top figure is the infrared pulse envelope and those in the bottom figure are the DSC curves of short exposures.

As clearly seen above, the response of DTA or DSC to the melting of a pure substance is different from the response to electric heating or infrared irradiation. The reason for the difference can be understood by examining the following fundamental equations of heat transfer. For transition and reaction the equation is

$$\lambda \nabla^2 T = \{ c_1 \rho_1 (1 - C) + c_2 \rho_2 C + \Delta H \rho f(C, T) \} \frac{\partial T}{\partial t} \quad (1)$$

where ∇^2 , λ , T , c , ρ , C , ΔH , $f(C, T)$ and t are respective-

ly a Laplacian operator, the thermal conductivity, the absolute temperature, the heat capacity, the density, the degree of conversion, the heat of transition or reaction, its rate as a function of C and T and time. The subscripts 1 and 2 denote the states before and after the transition or the reaction. For melting of a substance containing impurities, the following equation holds on the assumption of quasi-equilibrium and vant Hoff's equation;

$$\lambda \nabla^2 T = \left\{ c_1 \rho_1 \frac{T_M - T}{T_0 - T} + c_2 \rho_2 \frac{T_0 - T_M}{T_0 - T} + \Delta H \rho \frac{T_0 - T_M}{(T_0 - T)^2} \right\} \frac{\partial T}{\partial t} \quad (2)$$

where T_M and T_0 are the melting temperature of the pure substance and the maximum melting temperature of the substance containing impurities. For the reaction process we have;

$$\lambda \nabla^2 T = \left\{ c_1 \rho_1 (1 - C) + c_2 \rho_2 C + \Delta H \rho A \exp\left(-\frac{\Delta E}{RT}\right) g(C) \right\} \frac{\partial T}{\partial t} \quad (3)$$

where A , ΔE , R and $g(C)$ are respectively the pre-exponential factor, the activation energy, the gas constant and a function expressing the reaction mechanism, such as $(1 - C)^n$.

On the other hand, Eq. (4) holds in the case of electrical heating;

$$\lambda \nabla^2 T = c \rho \frac{\partial T}{\partial t} - q \quad (4)$$

where q is the power. By comparing Eqs. (1), (2) and (3) with Eq. (4), the essential difference is found. There are non-linear terms in Eqs. (1), (2) and (3), especially the third terms in the brackets of the right sides, while Eq. (4) is a linear equation. The additivity or the superposition principle found in the cases of electrical heating and infrared irradiation is caused by this linearity. This can not hold in the melting process because of non-linearity expressed in the fundamental equations. For transition and reaction, linearity can hold only when the change of temperature or heat-flow to the sample is integrated to measure the heat of the transition and reaction by DSC and quantitative DTA;¹¹⁾ i.e., fundamental equation is

$$\lambda \int_{t_i}^{t_f} \nabla^2 T dt = c \rho \int_{t_i}^{t_f} \frac{\partial T}{\partial t} dt + \Delta H \rho \int_{t_i}^{t_f} f(C, T) dt \quad (5)$$

where t_f and t_i are respectively the time of commencement and completion of the transition or the reaction. The heat capacity per unit volume is assumed to be

constant during the transition or the reaction. By subtracting a similar fundamental equation applied to temperature at the symmetrical point of the reference materials, we obtain the next linear equation;

$$\lambda \int_{t_i}^{t_f} \nabla^2 \Delta T dt = \Delta H \rho \quad (6)$$

where ΔT is the temperature difference.^{11,15)}

On the other hand, the triangular melting curve in the theory of O'Neill is derived on the assumption that the heat capacity is negligible. The triangular melting curve is derived, when the temperature gradient within the sample can be neglected in comparison to the temperature gradient outside the sample. Therefore, the temperature of the sample is constant and equals the melting temperature. Because of these serious assumptions, the validity of the theory is limited. To apply the method based on this theory, one should examine experimentally the apparatus with ultra pure substances for constancy of the slope of DSC melting curves as well as for the proportionality of the peak height to the square root of the sample weight. In a mathematical sense, the triangular melting curve is a solution of the fundamental equation at a discontinuous singular point. The above situation accounts for the decrease in accuracy of a DSC purity determination with increasing impurity level using the triangular melting curve technique.

It is apparent that the two approaches discussed in this paper are limited in their applicability. The linear theory of control and measurement can not be applied to DSC and DTA curves of transition and reaction, because of non-linearity of the phenomena measured. The method of temperature correction using the triangular melting curve can be applied in a limited area, where the temperature gradient within the sample is negligibly small in comparison to the outside temperature gradient. This condition has been attained using

agitation of the sample solution.¹⁶⁾ Also, the heat capacity must be negligibly small compared to the rate of heat evolution or consumption due to the transition or reaction.

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