



## **CLOSER RELATION BETWEEN THERMAL ANALYSIS AND CALORIMETRY**

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### **Abstract**

Several DTA experiments followed by calorimetric works are reviewed here to emphasise the importance of complementary role of both techniques. The thermal analysis is advantageous in the sense that it gives quickly the overall view of thermal behaviour of a material under various conditions. Calorimetric work provides accurate heat capacity data which enable to derive thermodynamic functions including the enthalpy and entropy. The latter quantity is especially important in judging whether the material obeys the third law of thermodynamics. However, calorimetric work leads occasionally to an erroneous conclusion if the work is not preceded by thermal analysis performed under various conditions. Sometimes, quality of information obtained by DTA exceeds that obtained by laborious calorimetry.

**Keywords:** calorimetry, DTA

### **Introduction**

Seven years ago, we have welcomed the hundredth anniversary of the memorial paper on the foundation of modern thermal analysis published by Le Chatelier. Prototype of the modern adiabatic calorimeter was developed in the same era. However, both of the methods have been developed independently without obvious reasons. Scientists engaging in respective fields aimed at characterisation of thermal behaviour of condensed matters. The compartmentalisation of scientific meetings in each specialised field tended to inhibit mutual exchange of useful information.

Somebody said that calorimetrists and thermal analysts had no common languages. Whoever mentions it, the statement is not true at all. I have started my

scientific works by construction of a fully automated DTA apparatus [1] around 1956 when there was no commercial apparatus. We found many phase transitions by this apparatus. Then we developed a low temperature adiabatic calorimeter [2] in order to measure the heat capacity of material which exhibited an interesting phenomenon as revealed by DTA. I will be one of a few scientists who know both the advantageous and disadvantageous aspects of the two methods. In what follows, some experimental results which clearly show the importance of close contact between the thermal analysis and calorimetry are described.

### Discovery of glassy crystals

DTA apparatus can be modified easily to detect the dielectric loss of any polar material if a sample is placed in an alternating electric field of high frequency [3]. When the reorientational frequency of the dipolar molecule becomes comparable to the frequency of external field, a part of electrical energy is transferred to the specimen and changed into thermal energy which raises the sample temperature. The temperature rise is proportional to the imaginary part of dielectric permittivity ( $\epsilon''$ ), square of the amplitude and frequency of the ac field. If the intensity of field is kept constant over a range of scanning temperature, the temperature rise is proportional to the dielectric loss of the sample.

Glycerol can be cooled down without any indication of crystallisation to produce ultimately a glassy liquid. The dielectric loss as is manifested by exothermic peak shifts to lower temperature as the frequency of electric field is lowered. A slight endothermic peak at 200 K is independent of the field and corresponds to the familiar glass transition. Extrapolation of the loss peak temperature to 200 K shows that the  $T_g$  value corresponds to the dielectric relaxation time of *ca.* 1 ks, which is the time scale of a single heat-capacity determination.

Cyclohexanol is crystallised at room temperature to form a fcc phase with molecules in orientationally disordered state. The fcc phase is easily undercooled by by-passing transformation into a low-temperature ordered phase. The situation is analogous to glass-forming liquids. Similar dielectric relaxation can be observed in the metastable fcc phase depending on frequency. A glass-like transition with relaxational nature appeared at around 150 K. Again the temperature ' $T_g$ ' corresponds to the dielectric relaxation time of 1 ks. The glass transition in crystalline phase embarrassed us at that time, since the glass transition has been regarded as one characteristic property of liquids possessing aperiodical structure. The heat capacity of cyclohexanol had been measured already by Kelley [5]. By a loop calculation of the entropy, he concluded that the

undercooled fcc phase was fully ordered at 0 K. This conclusion seems to be incompatible with the relaxation nature of the anomalous heat-capacity jump, as revealed by the DTA experiment. If we anneal the undercooled fcc phase below ' $T_g$ ', we can expect that the phase retains a negative entropy at 0 K.

The heat capacity was remeasured carefully and the results are summarised in Fig. 1 [6]. It turned out that the undercooled fcc phase had a residual entropy which is a manifestation of non-ergodic nature of the system. Enthalpy relaxation was observed at around  $T_g$ . We had to conclude that the heat-capacity jump at 150 K was essentially due to glass transition associated with freezing out of reorientational motion of the molecules in the fcc lattice. Thus, cyclohexanol is crystalline in the sense that it shows sharp fusion process and gives Laue spots to an incident X-ray beam. Cyclohexanol is liquid in the sense that it exhibits the residual entropy and glass transition.

The name 'glassy crystals' [7] was given to the crystalline substances possessing some degrees of freedom in frozen-in disordered state owing to prolongation of relaxation time for the relevant motion. In the case of ethanol [8], two kinds of frozen state were found for its liquid and for its orientationally disordered crystal. Determination of the entropy was preceded by DTA experiments carried out under various conditions. The study revealed that the glassy state of liquid is realised only by cooling of the liquid with a rate more than  $50 \text{ deg}\cdot\text{min}^{-1}$ . These observations justify the validity of regarding the glass transition as wide occurrence in condensed matters irrespectively of aperiodical spatial arrangement of the molecules. The glass transition should occur in any disordered systems whenever the relaxation time for relevant motion crosses the time scale of experimental probe. In this way, the initial DTA experiments played an essential role in finding out a new state of aggregation of molecules involving contradicting concepts.

## Radiation-induced solid-state polymerisation

Solid-state polymerisation of monomer induced by irradiation of high energy particle was one topic in the field of polymer science around 1965. Barkalov *et al.* [9] were interested in a possibility of the process in glassy state. They constructed a low temperature calorimeter with a built-in electronic gun for irradiation and applied it to vinyl acetate VAc known as a glass-forming liquid. They measured the enthalpies of crystallisation and fusion for two samples; one is pure and the other irradiated at 77 K. If the process occurs either during crystallisation or fusion on warming, the corresponding enthalpy change should be affected by the enthalpy of polymerisation. From the immutability of the enthalpy changes for both samples, however, they concluded that the polymerisation proceeded in the glassy state solely during the irradiation at 77 K.

This conclusion seems to be hard to accept because the temperature 77 K is far below its  $T_g$  (125 K). In such a state, the molecules are highly immobilised and cannot rearrange themselves to induce the in-source polymerisation. They ignored, however, a possibility that the polymerisation might occur just above  $T_g$  where the molecular mobility is recovered. Our DTA measurement [10] actually proved that it was really the case.

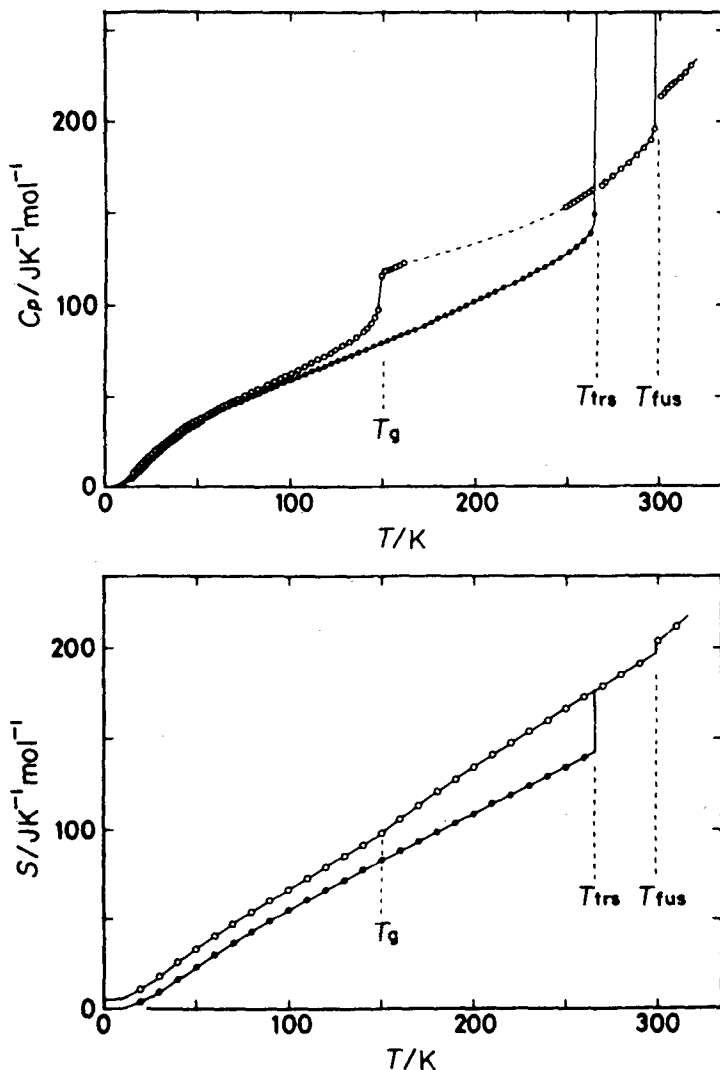


Fig. 1 Molar heat capacity and entropy of cyclohexanol

Figure 2 gives several DTA curves of pure (No.1) and irradiated (No. 2~7) VAc samples. The numbers in parentheses show polymer yield determined after

each experiment. Glass tube containing VAc sample was irradiated at 77 K by electron beam from Van de Graff and then placed quickly into a Cu block kept at 77 K. All the DTA experiments were carried out in the dark in order to avoid photolytic conversion of primary radical species. The pure sample exhibited the glass transition at 125 K, crystallisation at 148 K, and fusion at 180 K. For all the irradiated samples, additional exothermic peaks appeared just above  $T_g$ . The effect became prominent with the increase of polymer yield. In contrast to this, the enthalpy of crystallisation and of fusion decreased progressively and became complicated for heavily irradiated samples.

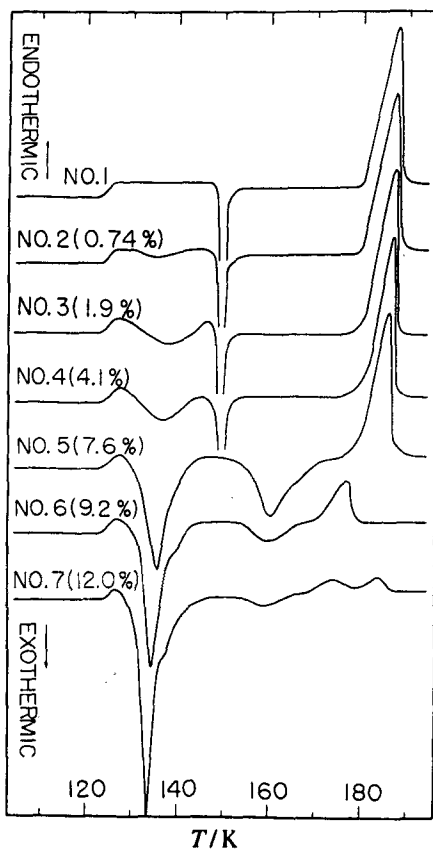


Fig. 2 DTA curves of vinyl acetate for pure (No.1) and electron-beam irradiated (No.2~7) samples

These results, supported by other findings, indicate clearly that VAc does not polymerise during irradiation in the glassy state but does at temperatures just above  $T_g$ , *i.e.*, in the undercooled liquid state. The molecules in the glassy state are too firmly immobilised to make a large scale rearrangement with respect to

their positions and orientations necessary for the polymerisation reaction to take place.

## Characterisation of non-crystalline solids

Non-crystalline solids can be prepared by many methods other than the conventional liquid-quenching. Some chemical reactions give non-crystalline products. For example, arsenic ions in aqueous solution react with  $\text{H}_2\text{S}$  gas to produce non-crystalline  $\text{As}_2\text{S}_3$ . The precipitates were found by our DTA experiment to exhibit a glass transition at 477 K [11]. The temperature is essentially the same with that of liquid-quenched sample. Likely, anhydrous magnesium acetate prepared by dehydration of its tetrahydrate crystal exhibited a glass transition at 469 K [12]. These are the first successful observations of the glass transition in non-crystalline solids produced by methods other than the liquid-quenching.

Grinding of crystalline substances gives sometimes non-crystalline solids. For example, tri-O-methyl- $\beta$ -cyclodextrin [13] can be amorphised by mechanical grinding of the crystal sample at room temperature and the non-crystalline solid exhibits a glass transition at 352 K, which is followed by crystallisation and fusion. This, along with the solid state amorphisation of crystals by irradiation of high energy neutron beam, is the process from opposite side against the conventional method. The former process implants excess energy to excite the equilibrium crystal and freezes it in an energised non-crystalline state. Naturally these procedures are necessary to carry out at temperatures below  $T_g$ . On the other hand, the latter is a process by which the kinetic energies of the constituent entities in a disordered phase are removed rapidly until it reaches a frozen-in disordered state below  $T_g$ .

Vapour deposition [14] has been established as a powerful method for producing non-crystalline solids from the vapour phase, the most disordered state of aggregation of molecules. This is because the method enables to extract the kinetic energies by molecule-to-molecule fashion from its vapour to produce non-crystalline solid without passing through the 'crystallisation dangerous region' in undercooled liquid. Thus any liquid with poor glass-forming ability can be vitrified in principle by this technique. Our DTA apparatus [15] for vapour deposition used liquid helium as a coolant. Sample vapour is deposited to one of the substrates kept at 4.2 K so slowly that the estimated cooling rate is roughly  $10^6 \text{ deg}\cdot\text{s}^{-1}$ .

Many substances were obtained successfully as non-crystalline solids in this way. One feature of the vapour-deposited non-crystalline solids is that the DTA curves exhibited exothermic base-line shift immediately after the heating experiment. The effect was considered first as a simple base-line shift due to dif-

ference in the heat capacities between the sample and reference cells. The sample cooled just before it reached  $T_g$  did not show anymore the base-line shift in the subsequent heating run. A low-temperature enthalpy relaxation that takes place far below the  $T_g$  for the vapour-deposited sample was conjectured.

An adiabatic calorimeter for vapour-deposited sample [16] was constructed to quantify the possible enthalpy relaxation rate that occurs at cryogenic temperatures far below the Kauzmann temperature [4]. A sample vapour of butyronitrile [17] was deposited extremely slowly at 40 and 67 K, respectively. Both of the vapour-deposited (VD) and liquid-quenched (LQ) samples exhibited the glass transition at 97 K. From the quasi-equilibrium heat capacity data alone, we cannot evaluate the difference in relaxation behaviour. However, the configurational enthalpy calculated by integrating the rate of enthalpy relaxation with respect to time was found to differ much between the LQ and VD samples. Figure 3 draws the excess enthalpy that each non-equilibrium sample possesses in the glassy state. The excess configuration enthalpy of the VD sample is much higher than that of the LQ sample. For the VD sample deposited at 40 K, the configurational enthalpy amounts to  $1.33 \text{ kJ}\cdot\text{mol}^{-1}$ , compared with  $0.08 \text{ kJ}\cdot\text{mol}^{-1}$  for the LQ sample, indicating the formation of a non-crystalline solid with high excess enthalpy by the vapour deposition method. The enthalpy relaxation was found to occur from much lower temperature for the VD samples than that for the LQ sample. The rate of enthalpy relaxation of the VD sample observed at three different temperatures showed highly non-exponential behaviour. Such a non-exponential relaxation is known to be a characteristic feature of LQ non-crystalline solids observed around the glass transition region [14].

A variety of experiments have shown that the approach of any physical quantities from non-equilibrium to the equilibrium value can be expressed over a period of time by the Kohlrausch-Williams-Watts (KWW) function [18, 19],

$$\varphi(t) = \varphi(0) \exp [-(t/\tau)^\beta],$$

where  $\varphi$  is the relaxation function,  $\tau$  the effective relaxation time, and  $\beta$  an adjustable parameter. Obviously  $\beta = 1$  corresponds to exponential approach. Therefore, the quantity  $\beta$  reflects the non-exponential nature of the relaxation and is called the fractional exponent. This equation has been applied hitherto to glassy liquids at modest departure from the equilibrium, but the present analysis showed that the equation is applicable likely to the enthalpy relaxation for the VD sample far apart from the equilibrium. The exothermic enthalpy relaxation process was analysed well in terms of the KWW equation. Here, the relevant relaxation function  $\varphi$  is excess enthalpy  $\Delta H(t)$  of non-equilibrium sample over that of the equilibrium liquid. All the data gave straight lines at the respective temperature studied. The exponent  $\beta$  at 83.8 K is 0.07, being quite differ-

ent from unity. As the temperature is raised, the value  $\beta$  increases to 0.11 at 89.7 K and 0.21 at 95.0 K. These values are quite different from the values typically observed in LQ non-crystalline solids near the equilibrium liquids.

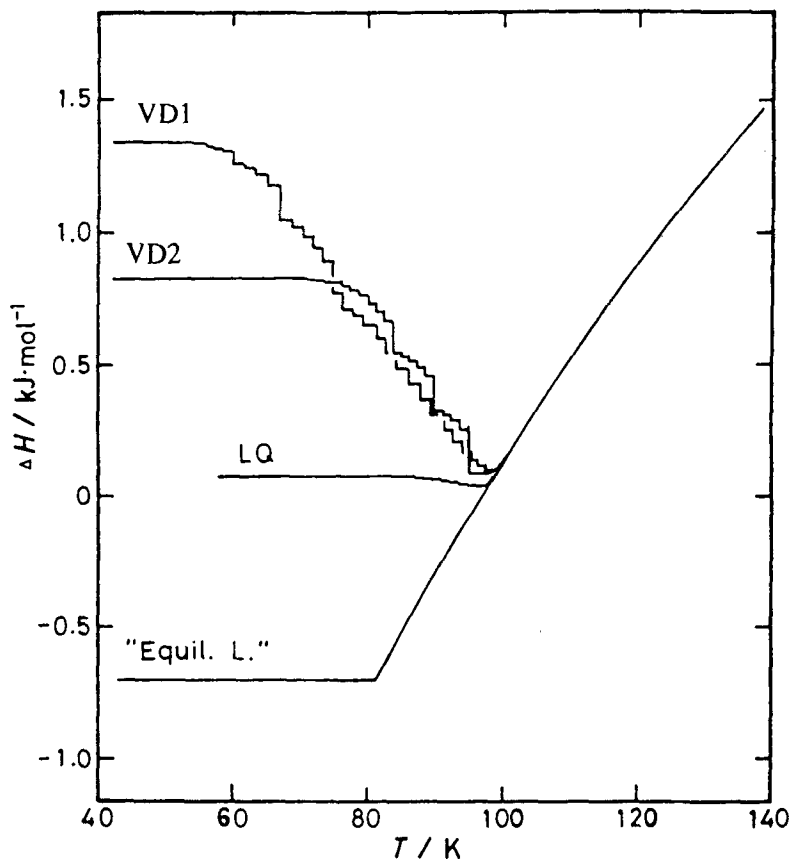


Fig. 3 Configurational enthalpies of butyronitrile for vapour-deposited (VD) and liquid-quenched (LQ) samples

### Grey zone between 4 and 300 K

Scientists engaging in material sciences interpret usually their observed properties based on the crystal structure. Low temperature physicists and chemists are not the exceptional case. Magnetic properties can be clarified by seeking special interaction path in the determined structure. Unfortunately, however, the information of structure is available only at room temperature in most cases. This situation induces sometimes erroneous conclusion. Here, one example of this kind of misleading picture is described based on our experience.



A polynuclear complex salt,  $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})]\text{Cl}\cdot 3\text{H}_2\text{O}$ , is known to show anomalous magnetic behaviour at cryogenic temperatures. Wucher and Gijsman [20] reported that the anomalous behaviour of the magnetic susceptibility and heat capacity could be explained by an isosceles triangle model with respect to the three  $\text{Cr}^{3+}$  ions cluster. Thus the Hamiltonian is given by

$$H = J_0(S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_1) + J_1(S_2 \cdot S_3),$$

where  $S_1$ ,  $S_2$  and  $S_3$  are the spin operators,  $J_1$  an adjustable exchange parameter reflecting the extent of deviation of the cluster from the equilateral triangle. Later, the crystal structure of this compound was determined at room temperature [21]. Three  $\text{Cr}^{3+}$  ions were found to form an equilateral triangular cluster. From this crystallographic information, Uryu and Friedberg [22] objected to the interpretation by Wucher and Gijsman based on the isosceles triangle model and proposed a different Hamiltonian of a novel type. The Hamiltonian was, however, objected by another scientist by virtue of its non-Hermiticity. Thus there were controversial discussions about the scheme of the magnetic interactions in this crystal.

The confusing situation was resolved by a simple DTA experiment which showed an existence of a first order phase transition at 211 K in this compound. The subsequent heat capacity measurement showed that the enthalpy and entropy changes associated with the transition were  $3.322 \text{ kJ}\cdot\text{mol}^{-1}$  and  $13.78 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , respectively [23]. Many new peaks appeared in IR spectra in the low temperature phase, indicating lowering of local symmetry at various sites where the ions or molecules are situated. Magnetic heat capacity at low temperatures obtained by subtracting the contributions from the lattice vibration is drawn in Fig. 4. The magnetic heat capacity is well reproduced by the combination of half moles of isosceles triangle cluster with  $J_1 = 4.5 \text{ K}$  and the remaining half moles with  $J_1 = -1.5 \text{ K}$ . From these experimental findings, we concluded that the cluster ions possessing equilateral triangle at room temperature are slightly distorted through the phase transition to give rise two kinds of isosceles triangle cluster at low temperatures.

This kind of confusion occurs sometimes in the low temperature studies. Quick survey by DTA or DSC in the intermediate temperature region between 4 and 300 K saves unnecessary confusion and controversy. A brief survey of literatures concerning the transition phenomena in crystals showed that more than 95% of the listed materials exhibited the transition temperature either below 20 K or above 80 K. This reflects merely the lack of experimental study in the intermediate temperature range. For this purpose, we developed a low temperature DTA apparatus [24] workable above 20 K by using liquid hydrogen as a

coolant. The apparatus proved its usefulness by discovering a phase transition in tetrahydrofuran clathrate hydrate crystal at 62 K.

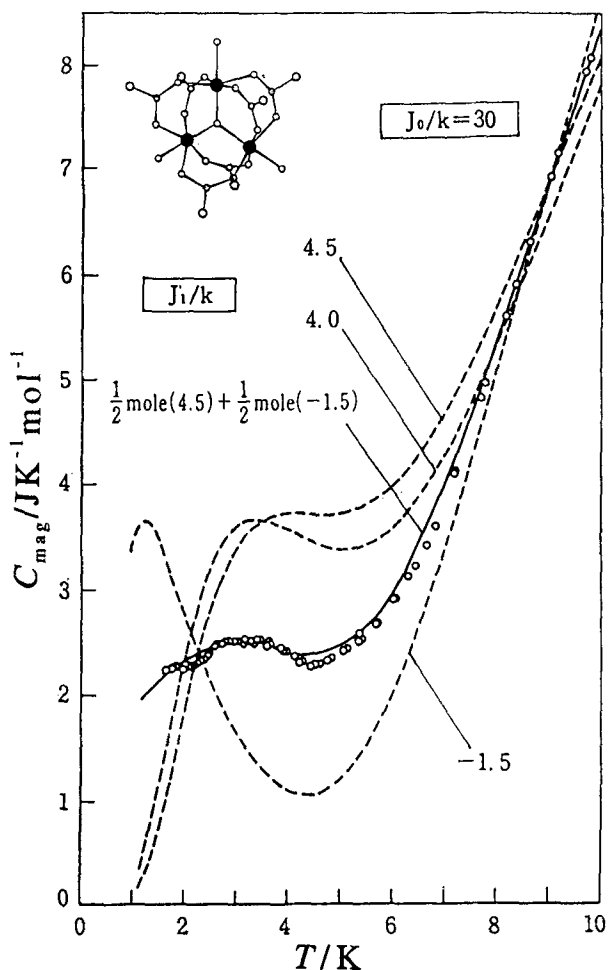


Fig. 4 Magnetic heat capacity of  $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})]\text{Cl}\cdot 3\text{H}_2\text{O}$  at low temperature

## Conclusion

Heat flow occurs through a variety of path; conduction, convection and radiation. Accurate control of the heat flow requires accumulation of special experiences. Construction of adiabatic calorimeter is, therefore, possible only by specialist with rich experience, careful design, expensive instruments, and skillful handling. It takes at least one year before reliable heat capacity data are obtained. This situation is in good contrast with the construction of DTA apparatus

with respect to the cost, duration and endeavour. Calorimetric experiment provides accurate thermodynamic data at the expense of a large amount of sample, laborious and time-consuming hard work. On the other hand, DTA experiment can be done within one day in most cases to provide the overall view of thermal behaviour of any materials. The obtained DTA curve gives immediately the information as to where a phase transition, glass transition, or fusion takes place. Once we enter into a wood, we can examine carefully individual tree, but we cannot see the whole view of the wood. Both the qualitative and quantitative studies can provide two aspects of the key to clarify the nature of material.

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**Zusammenfassung** — Es wird ein Rückblick auf verschiedene von kalorimetrischen Arbeiten gefolgt DTA-Experimenten gegeben, um die Wichtigkeit der einander ergänzenden Rolle beider Techniken zu betonen. Der Vorteil der Thermoanalyse besteht darin, einen schnellen Gesamtüberblick über das thermische Verhalten der Substanzen unter verschiedenen Bedingungen zu liefern. Kalorimetrische Arbeiten liefern präzise Wärmekapazitätsangaben, die eine Ableitung thermodynamischer Funktionen wie Enthalpie und Entropie ermöglichen. Letzterer Größe kommt besondere Bedeutung bei der Beurteilung zu, ob eine Substanz dem dritten thermodynamischen Gesetz unterliegt. Kalorimetrische Arbeiten können jedoch gelegentlich zu Fehlschlüssen führen, wenn keine Thermoanalyse unter verschiedenen Bedingungen vorangeht. Manchmal gehen die mittels DTA erhaltenen Informationen über die mittels Kalorimetrie ermittelten hinaus.