

INTERPLAY OF CALORIMETRY AND THERMAL ANALYSIS

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ABSTRACT

Many types of DTA and calorimetric equipments with general and special purposes have been developed in our laboratory. The DTA apparatuses have been utilized to survey rapidly the general feature of thermal behavior of a sample prior to the laborious and time-consuming calorimetric measurement. Sometimes the DTA experiment exceeded the calorimetric work in the sense that the calorimetric work without any previous thermal characterization brought about an erroneous conclusion. Some selected topics which clearly prove the usefulness of the DTA experiment performed in the early stage of thermodynamic research are reviewed here, emphasizing the complementary role of both the experimental methods.

INTRODUCTION

One topic in material science is appearance of metastable modification occurring in many organic as well as inorganic compounds. Full clarification of the condition of appearance is very important, because ignorance of this factor causes some confusion in the description of static and dynamic properties of the material. The following three examples of the formation of metastable phase were observed first by DTA experiment, and the following calorimetric works were focussed on the most interesting points clarified by the DTA study. A recent discovery of an ordering transition in THF hydrate crystal doped with a trace amount of KOH is also reported. The dopant accelerated drastically the reorientational motion of water molecules connected by hydrogen bonds to form polyhedral cages, and induced the first order phase transition in otherwise frozen-in

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disordered host cages. The situation is quite similar to the case of hexagonal ice[1].

EXPERIMENTAL

Ferrocene

Ferrocene has been accepted as one of the key substances of organometallic compounds. The crystal exhibits a λ -type transition at 164 K due to an order-disorder process of cyclopentadienyl ring. In the course of our reinvestigation of the phase transition by DTA method (Fig. 1), we have found unexpectedly a new low temperature phase(LTP), which can exist stably below 240 K [2]. The stable LTP transforms to HTP with considerable superheating effect. Conversely the HTP is easily undercooled and the λ -type phase transition occurs in the undercooled metastable phase. There have been more than ten groups who were engaged in the ferrocene problem, but none of them has noticed the presence of the stable LTP. Heat capacity and the derived entropy diagrams are given in Fig. 2 [3]. A loop calculation showed that the undercooled HTP

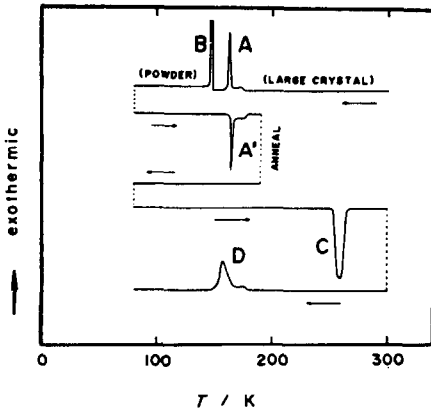


Figure 1 (top) DTA curves of ferrocene crystal

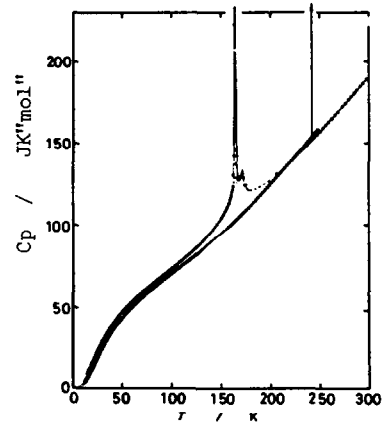
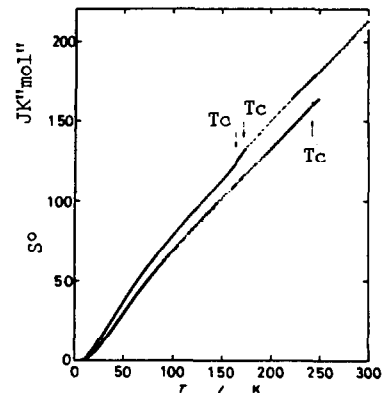


Figure 2 (right) Molar heat capacity and entropy of ferrocene



as well as the new LTP obeyed the third law of thermodynamics.

Ethanol

Incorrect observation of glass transition of ethanol is again due to the metastability problem [4]. Since the calorimetric works done fifty years ago, ethanol has been accepted as a typical glass-forming liquid. But our remeasurement using DTA showed that the description is not correct. Our experiment tells us that an extremely rapid cooling of liquid with a rate more than 50 K min^{-1} is necessary to obtain the glassy liquid. If the cooling rate is moderate as normally used in the low-temperature calorimetry, say 2 K min^{-1} , a metastable crystal is formed first which goes over to glassy crystalline state through another glass transition. Accidentally both the glass transitions occur at essentially the same temperature. Accurate heat capacity measurement showed that the heat capacity data for "glassy liquid" of the previous workers correspond to those of our "glassy crystals". The heat capacity of the undercooled liquid is much higher in magnitude than their

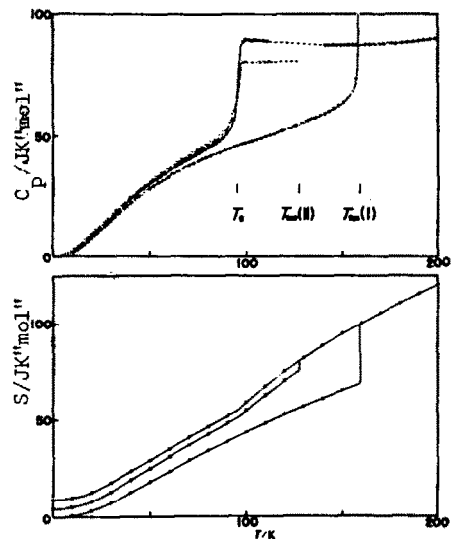
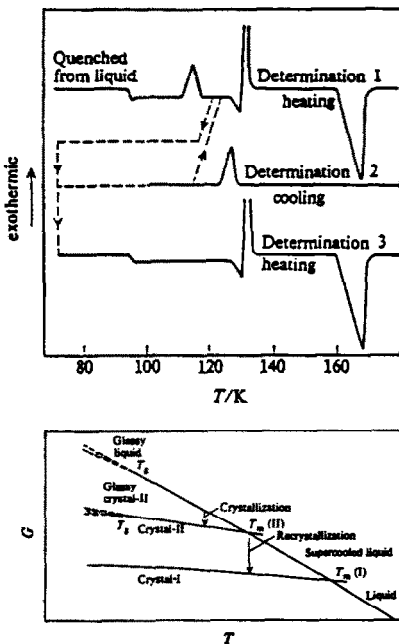


Figure 3 (left) DTA curves and schematic diagram of various phases of ethanol.

Figure 4 (right) Molar heat capacity and entropy of ethanol.

values and can be connected smoothly to the stable liquid above the melting temperature. Residual entropy for the glassy crystal ($4.24 \text{ JK}^{-1}\text{mol}^{-1}$) is almost half of that for the glassy liquid ($8.93 \text{ JK}^{-1}\text{mol}^{-1}$), indicating smaller scale of the frozen-in disorder.

dl-Camphor

Both d- and dl-camphor are orientationally disordered crystals (hexagonal) at room temperature. On cooling they transform into ordered phase. d-Camphor transforms at 244 K into a tetragonal phase through a first order transition, while racemic camphor shows higher order transition at 204 K with keeping the same structure.

Our DTA experiment showed anomalous transitional behavior for racemic camphor [5]. The transition temperature depends strongly on the annealing taken below the apparent transition region. The transition temperature moved about 10 K by simple annealing (Fig. 5) and this explained why the literature values of the transition temperature of racemic camphor scattered widely, in contrast to that of d-camphor. In order to understand this unusual behavior, it is necessary to remind the fact that the racemic modification is an equimolecular mixture of the two enantiomers. There seem to exist two kinds of ordering processes in di-camphor taking place around the

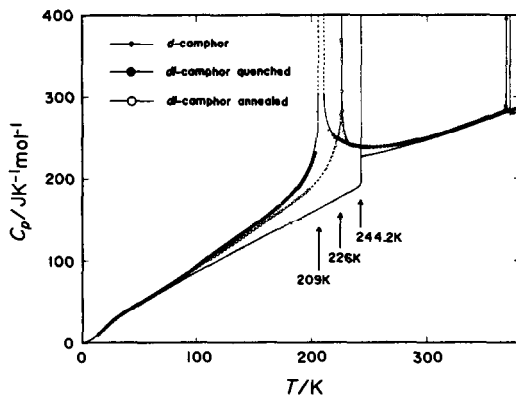
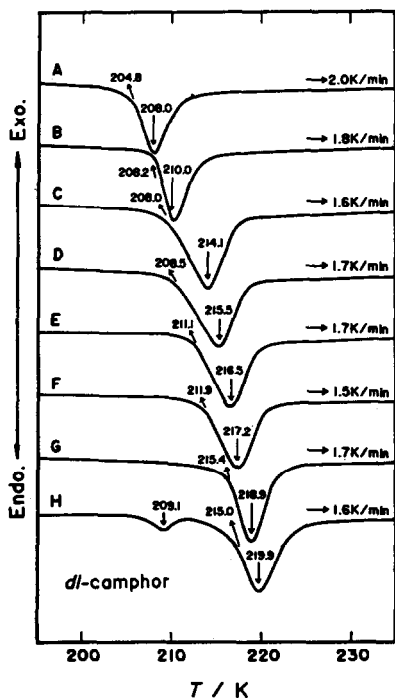


Figure 5 (left) DTA curves of dl-camphor.

Figure 6 (top) Molar heat capacities of d- and dl-camphor.

apparent transition temperature, each possessing completely different time scale.

Heat capacity measurement on racemic camphor was performed on quenched and well annealed (~ 1 month) specimens. The difference of transition temperatures amounts roughly to 17 K. The well annealed specimen removed the entropy by $1.6 \text{ JK}^{-1}\text{mol}^{-1}$ from the quenched specimen possessing still some kind of positional disorder.

THF hydrate

Glass transition is essentially a freezing phenomenon occurring in some disordered system owing to prolonged relaxation time at low temperatures. Glass transition was found, therefore, to occur not only in metastable phase but also in stable crystalline phase. One famous example of the latter is hexagonal ice, for which half-hydrogen statistical disorder associated with hydrogen bonding freezes at low temperature before a hypothetical transition temperature is reached on cooling. A trace amount of KOH doped into the ice lattice was found to accelerate dramatically the proton configurational rearrangement [1]. The dopant removed the kinetic barrier and induced a first order phase transition at 72 K, removing a substantial fraction of the residual entropy observed by Giauque and stout in 1936 for the first time.

The same technique was applied recently to tetrahydrofuran

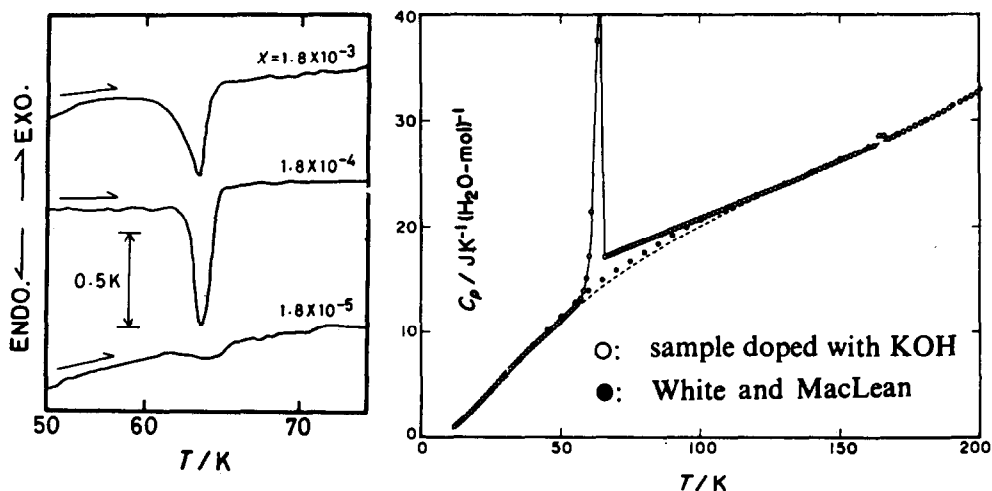


Figure 7 (left) DTA curves of THF hydrate doped with KOH.

Figure 8 (right) Molar heat capacities of THF hydrate, pure and doped specimens.

(THF) hydrate crystal [6]. A home-made DTA apparatus was constructed for this purpose using liquid hydrogen as a coolant [7]. A DTA experiment showed a transition phenomenon at 62 K which was not detected in a previous calorimetric work on pure specimen. This is the first successful observation of ordering phenomenon in clathrate hydrates which contain polyhedral cages made of hydrogen-bonded water molecules and guest molecules enclathrated in the cages.

CONCLUSION

All these experiences stress the importance of complementary role of calorimetry and thermal analysis in solving a particular physico-chemical problem. Qualitatively interesting points disclosed by the preliminary DTA experiment which can be done rapidly should be spotlighted by the following calorimetric work with quantitative nature. Both the qualitative and quantitative studies constitute two aspects of the key in opening new field of every branches of science.

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