

## **A LOW-TEMPERATURE DTA APPARATUS FOR TEMPERATURES DOWN TO 15 K AND THERMAL ANOMALIES IN 3-METHYL-1-BUTENE AND THF HYDRATE \***

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### **ABSTRACT**

A low-temperature DTA apparatus was constructed for studies below 80 K using liquid hydrogen as coolant. The principle follows that of the conventional type used above liquid nitrogen temperature. The performance of the apparatus was examined by a test run for crystalline  $\text{ND}_4\text{HgCl}_3$ . The phase transition at 58 K, whose enthalpy was known to be  $332 \text{ J mol}^{-1}$ , appeared as a sharp peak with a peak height of 0.3 K, and the noise level of the baseline was within 3 mK. A glass transition was discovered for liquid 3-methyl-1-butene at 67.4 K. This temperature was compared with those of the other hydrocarbons with five carbon atoms. A phase transition was discovered at 62 K for crystalline tetrahydrofuran (THF)·16.9H<sub>2</sub>O doped with a small amount of KOH.

### **INTRODUCTION**

Many methods are applied to the study of phase transitions and glass transitions. Differential thermal analysis (DTA), one of the simplest methods to operate, provides a powerful technique for detecting such transitions. It also plays a preliminary role for more accurate and/or more complicated measurements such as calorimetry, spectroscopy, and diffraction experiments. The use of sub-ambient temperatures was pioneered by Jensen and Beevers as early as 1938 [1]. Nowadays, many kinds of DTA apparatus are commercially available, all of which are limited to use above liquid nitrogen temperature, although at least one is claimed to be operable down to 4 K [2]. From the physico-chemical standpoint, however, studies on the properties of substances of simple molecular shape with weak intermolecular interactions are quite important. An interesting behavior is often expected to be seen at

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\* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.  
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relatively low temperatures for these substances. In this respect, the development of a DTA apparatus workable at temperatures below 80 K is highly desirable.

In this work we constructed such a DTA apparatus, and studied the thermal properties of two substances which could not be investigated with the conventional apparatus [3]. A glass transition and a phase transition were found in 3-methyl-1-butene and tetrahydrofuran · 16.9H<sub>2</sub>O doped with a small amount of KOH, respectively. The latter is particularly significant in view of the fact that it would give the first example of the phase transition due to the ordering of hydrogen atoms among all the gas hydrates that are kinds of ice polymorphs.

#### APPARATUS

The DTA apparatus follows, in principle, the conventional apparatus for use above liquid nitrogen temperature [3]. Figure 1 schematically shows the cryostat of the apparatus. The sample is charged in a sealed pyrex DTA tube

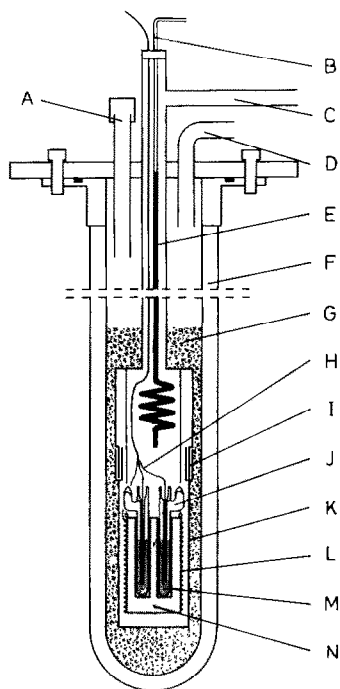


Fig. 1. Schematic drawing of the cryostat of the DTA apparatus. (A) Inlet for coolant, (B) sample-filling tube, (C) vacuum line, (D) outlet for coolant, (E) heater for the filling tube, (F) dewar, (G) coolant, (H) chromel-P-constantan thermocouple, (I) joint for the can, (J) DTA tube, (K) can, (L) heater for the block, (M) sample, (N) DTA block.

(8 mm OD) under 100 kPa of helium gas at 300 K. The cylindrical copper block N, 30 mm in diameter and 60 mm in length, has two 50 mm deep wells drilled at symmetrically related positions on the top, and the DTA tubes of the sample and benzene, as reference, are embedded in the respective wells. Chromel–P–constantan thermocouple H, with junctions in the bottom of the reentrant wells of the tubes, monitors the temperatures of the substances in the form of an electric signal, which is amplified with a microvoltmeter (Model AM-1001 from Ohkura Electric Co., Ltd.) and recorded on a strip chart. The absolute temperature of the sample is determined from the signal of another chromel–P–constantan thermocouple referred to 0°C outside the cryostat by use of a digital voltmeter (Model TR-6855 from Advantest Co., Ltd.).

Temperatures below 80 K are achieved by introducing liquid hydrogen into pyrex dewar F through an aperture of inlet A and a small quantity of helium gas into the inner space of can K through vacuum line C. When temperatures below the normal boiling point of the coolant are necessary, the space inside the dewar can be evacuated through an outlet pipe D for coolant. A DTA curve on cooling is obtained by adjusting the cooling rate with the amount of helium gas (ordinarily about 7 kPa at 80 K) used as a heat exchanger inside the can. The DTA run on heating, on the other hand, was started by passing a controlled electric current through heater L immediately after the level of the liquid coolant had left the bottom of can K. The sample tube was replaced by dismantling the can at a joint I. This is easily carried out by melting Wood's alloy at the joint.

Sample-filling tube B, made of stainless steel, is intended for studies on substances which are gaseous at room temperature. The bottom end of the tube should then be connected with the aperture of the DTA tube through a Kovar pipe. The coiled part of the filling tube was made of annealed copper tubing in order to allow appropriate adjustment of the position of the sample tube. Heater E is used to keep the temperature of tube B above the dew point during condensation of the sample into the DTA tube. DTA measurement of the condensed sample requires the same procedure described above in the case where the sample substance is in the condensed state at room temperature.

Figure 2 shows a test run taken to check the sensitivity and stability of the apparatus by using a sample of crystalline  $\text{ND}_4\text{HgCl}_3$ . This substance is known from a calorimetric study [4] to exhibit a  $\lambda$ -type phase transition with a weak first-order component at 58.26 K. Since the amount of sample used in the present thermal analysis is about a hundredth of a mole, only  $\sim 3$  J is excessively absorbed to yield the peak on the chart. The sample crystal was taken from the same batch as used for calorimetry [4]. The measurement was started at 53 K on heating at  $0.35 \text{ K min}^{-1}$  in the region of the phase transition. A clear endothermic peak appeared at 58.0 K on the curve. The temperature of the sample at the top of the peak was also the same (58.0 K)

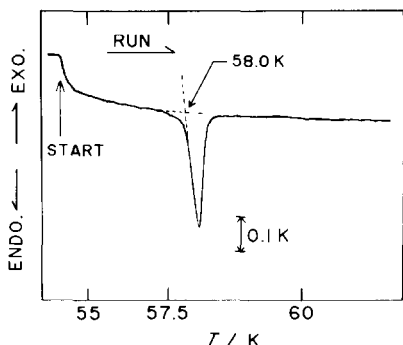


Fig. 2. DTA curve of  $\text{ND}_4\text{HgCl}_3$  crystal as a test run.

after correcting for the difference between the temperatures on the sample and the reference sides. The sensitivity is thus concluded to be sufficient for studies on most phase transitions, even with a small heat effect. The noise is within the level of 3 mK. This illustrates good stability of the baseline and an excellent signal-to-noise ratio. The sensitivity would, however, decrease at lower temperatures because of the decrease in thermopower of the thermocouple used; e.g., the thermopower at 15 K is 1/3 compared with that at 58 K. The use of iron-0.07% gold/chromel thermocouple would thus be better in the experiment below 40 K.

## EXPERIMENTAL RESULTS

### *3-Methyl-1-butene*

The glassy state can be achieved by cooling a liquid to low temperatures without crystallization. Glasses are usually formed with substances whose molecular shapes and/or intermolecular interactions are complex; e.g., organic polymers, covalent or ionic substances forming long-chain bonds, and hydrogen-bonded compounds [5]. This would be a reflection of the fact that the substances with these kinds of complications often fail to crystallize. Studies on rather simple compounds with weak Van der Waals' interactions are, however, important for further insight into the nature of the glassy state and the glass transition. Most of such DTA studies have been carried out above 80 K [6], except for those on vapor-condensed solids [7].

Figure 3 shows the result obtained for 3-methyl-1-butene with the present apparatus. The sample (reagent grade from Tokyo Kasei Kogyo Co., Ltd.) was purified by three consecutive vacuum distillations. The curve clearly shows the existence of a glass transition at 67.4 K which corresponds to about two-thirds of its melting temperature (104.65 K).

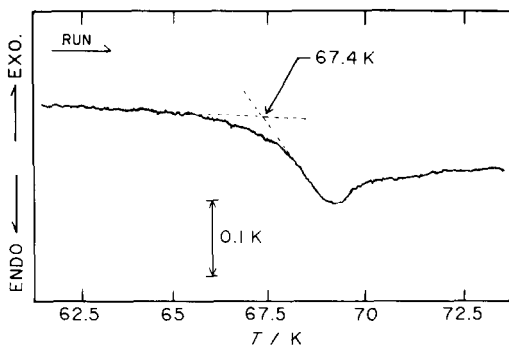


Fig. 3. DTA curve of 3-methyl-1-butene in the supercooled liquid state.

A glass transition is a kind of relaxation phenomenon. A drastic change in various physical quantities appears at the glass transition temperature at which the characteristic time for the configurational change crosses the experimental time scale, say 1 ks for a heat capacity measurement. 3-Methyl-1-butene is one of the hydrocarbons with five carbons in the molecule. It is interesting to compare its glass transition temperature with those for a homologous family of hydrocarbons which are different from each other in their nature of bonding and in their skeletal structures. The glass transitions were reported to occur at 65 K for isopentane [8] and at 69 K for n-pentane [9]. For 1-pentene, the temperature was recently determined in our laboratory to be 71.5 K [10]. All these hydrocarbons thus exhibit their glass transitions in the narrow temperature range 65–72 K.

A minor difference is found between the temperatures of isopentane and 3-methyl-1-butene, and between those of n-pentane and 1-pentene ( $\sim 2.5$  K each). It probably depends on whether the terminal C–C bond is single or double. Another systematic difference is found between 3-methyl-1-butene and 1-pentene, and between isopentane and n-pentane. The former substance gives a temperature lower by  $\sim 4$  K than the latter in both comparisons. This is probably due to the different positions of the carbon atoms, namely the skeletal structure of the molecule. The glass transition temperature for these hydrocarbons changes in the same systematic way.

### *THF · hydrate*

Water molecules can give rise to diverse three-dimensional hydrogen-bonded networks, each molecule forming a tetrahedrally disposed set of bonds. More than ten ice polymorphs have so far been confirmed taking the differences in the hydrogen atom positions into consideration. A gas hydrate may be considered as a kind of ice polymorph with its host lattice composed only of water molecules. Guest molecules, accommodated in the voids of the

host lattice, stabilize the structure by their rather weak Van der Waals' interactions with water molecules.

Most of the gas hydrates were identified prior to 1900, and their structures and properties have since been studied with increasing interest from both the academic and industrial standpoints. The possibility of exploiting natural gas resources deposited in the hydrate form has recently led to an increased activity in the study of these compounds. The gas hydrates are classified according to the structure of the host "ice" lattice: Von Stackelberg's structures I or II [11]. Structure I, which is formed by guest molecules of some 0.53 nm or less in diameter, consists of 12-hedral and 14-hedral cages each sharing pentagonal faces with one another; the composition is  $M \cdot 5.75H_2O$  if all the cages are filled with M. Structure II, formed by molecules with diameters in the range 0.56–0.66 nm, consists of 12-hedral and 16-hedral cages with pentagonal faces shared with one another; if only the larger cages are filled the composition is  $M \cdot 17H_2O$ . The hydrogen atoms are disordered in their positions as in some ice polymorphs of hexagonal ice Ih, cubic ice Ic, ice III, and so on. This has been convincingly shown by dielectric measurements [12].

We have so far studied the thermal properties of some ice polymorphs and Ar gas hydrate, all with three-dimensional hydrogen-bonded networks. Glass transition phenomena due to freezing of the configuration of hydrogen atoms were found to take place around 110 and 140 K for ice Ih [13] and Ic [14], respectively, while no anomaly was observed for the Ar gas hydrate in the temperature range 13–130 K [15]. Doping these substances with a small amount of KOH is believed to produce an ionized vertex together with an orientational defect in the lattice and hence greatly enhance the rate of rearrangement of the atoms. A glass transition in the Ar hydrate (not seen in the pure case) took place around 60 K [15] and the glass transition temperature of the doped sample of ice Ic decreased by about 30 K compared with that of the pure sample [14]. In the case of ice Ih, a first-order phase transition was found at 72 K, and the ordered arrangement of hydrogen atoms was realized for the first time [16].

In this section we show the result of thermal analysis on tetrahydrofuran · hydrate [ $THF \cdot 17H_2O$ ] doped with KOH.  $THF \cdot 17H_2O$  takes up the structure of type II as the host ice lattice composed of  $H_2O$  molecules. A calorimetric study on the pure substance was recently carried out by White and MacLean in the temperature range 17–261 K by the adiabatic method [17]. Neither a static nor dynamic anomaly in the thermal behavior was reported.

THF (Tokyo Kasei Kogyo Co., Ltd.) was purified by fractional distillation using a rectifier with more than 80 theoretical plates (Shibata Kagaku Kikai Co., Ltd.). No impurity was detected in the main part of the distillate by gas chromatography. KOH aqueous solution for volumetric analysis (Wako Pure Chemical Ind., Ltd.) was diluted to the desired mole fraction of

KOH with deionized distilled water. The THF aqueous solution corresponding to the hydrate  $\text{THF} \cdot 16.9\text{H}_2\text{O}$  was prepared by simply mixing the two liquids, whose quantities were determined gravimetrically. Three differently doped samples were prepared to examine the dependence of their thermal properties on the amount of dopant. In Fig. 4,  $X$  denotes the ratio  $n(\text{KOH})/[n(\text{H}_2\text{O}) + n(\text{KOH})]$ , where  $n$  stands for the amount of substance. The DTA tubes, each loaded with specified quantities of samples of different  $X$ , were sealed on the vacuum line after charging with He gas at 0.1 MPa. The three DTA curves in the figure were taken at the same heating rate. They clearly show the existence of a phase transition around 62 K. The transition temperature is independent of the mole fraction of KOH, indicating that the transition is a property intrinsic to the hydrate itself. The phase transition is considered to have escaped observation in calorimetry using a pure specimen for kinetic reasons, and to appear due to the catalytic action of the dopant. Differences in both the shape and magnitude of the peak, however, reveal the dependence of the transition on the amount of KOH. The curve for  $X = 1.8 \times 10^{-4}$  gave rise to the sharpest peak of the three. The amount of KOH for  $X = 1.8 \times 10^{-5}$  is definitely insufficient to transform the majority of the sample into the low-temperature form at least without long annealing, though the fraction of the transformed region was large enough to exhibit an appreciable endothermic signal beyond the noise level on the curve. The endothermic effect for  $X = 1.8 \times 10^{-3}$ , on the other hand, made a slightly broad peak exhibiting a long tail on the low temperature side in comparison with that for  $X = 1.8 \times 10^{-4}$ . The peak areas, which are roughly proportional to the enthalpies of transition, are essentially the same for the two curves with  $X = 1.8 \times 10^{-3}$  and  $1.8 \times 10^{-4}$ . Too much doping of

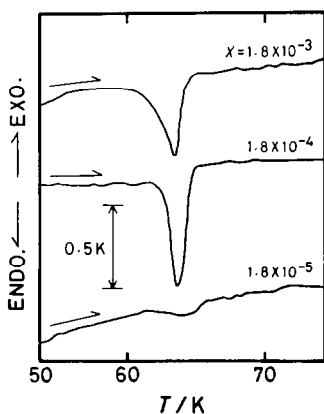


Fig. 4. DTA curves for crystalline  $\text{THF} \cdot 16.9\text{H}_2\text{O}$  doped with small amounts of KOH. For each curve  $X$  denotes the mole fraction of KOH,  $n(\text{KOH})/[n(\text{H}_2\text{O}) + n(\text{KOH})]$ , where  $n$  is the amount of substance.

the hydrate with KOH might cause some scatter of the transition temperature.

In conclusion, the phase transition of  $\text{THF} \cdot 16.9\text{H}_2\text{O}$  crystal was discovered by doping the hydrate with a small amount of KOH. The transition takes place at 62 K, around which no heat capacity anomaly was observed in previous calorimetric work [17] on the pure sample. The presence of KOH in the crystal induced a phase transition even in a gas hydrate with a dipolar guest molecule. The phase transition may be attributed to the ordering of hydrogen atoms involved in the three-dimensional hydrogen-bonded network, as in the case of hexagonal ice Ih. It is hard to imagine that the KOH doping in the hydrate crystal induces rotational transition of the guest molecules. Another possibility is that the observed phase transition is associated with the simultaneous order-disorder processes with respect to the position of the hydrogen atom and the orientation of the tetrahydrofuran molecule. Reorientational motion of the water dipoles produces a fluctuating electric field and affects the reorientational motion of the guest dipoles which, in turn, affects the reorientational motion of the water molecules. The coupled motion will eventually lead to a cooperative ordering of the host and guest molecules. This conjecture is probable in view of the fact that the argon hydrate crystal doped with KOH shows no phase transitional behavior [15]. Accurate calorimetry and other studies on the doped sample are now under way.

## CONCLUSION

The newly designed low-temperature DTA apparatus was confirmed to have both a high sensitivity and a low noise level for the baseline. In addition to a satisfactory result on the test sample  $\text{ND}_4\text{HgCl}_3$ , a glass transition which manifested itself as a jump in heat capacity was clearly shown on the curve for liquid 3-methyl-1-butene. Particularly valuable information was obtained with this apparatus for crystalline  $\text{THF} \cdot 16.9\text{H}_2\text{O}$  doped with KOH. The phase transition at  $\sim 62$  K is possibly ascribed to the ordering of hydrogen atoms. If this is the case, the present observation will lead to more extensive studies on gas hydrates, and the structure and properties of the ordered phase will be raised to the stage of experimental research.

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