Thermodynamic properties and phase transformations in methylhydrazine monohydrate

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Abstract

Liquid methylhydrazine monohydrate ($CH_3NHNH_2 \cdot H_2O$; molar mass $= 0.06409$ kg mol^{-1}) can be easily quenched into a glassy state. On reheating, the glass transition occurs near 160 K (T_g) with an important heat capacity variation ($\Delta C_p = 96.8$ J mol^{-1}K^{-1}). This glass is extremely "fragile" according to Angell's classification.

Depending on the thermal treatment, this glass transition is followed by successive phase transformations with slow and complex kinetics which are described here in detail.

Thermodynamic properties were investigated by means of adiabatic calorimetry.

Enthalpies and heat capacities were determined or extrapolated from 100 K to 265 K for the glassy state and all condensed phases: the liquid, the undercooled liquid, the metastable and the stable solid phases. The melting temperature $T_{fus,s}$ and the melting enthalpy $\Delta H_{fus,s}$ for the stable solid phase were estimated to be 234 K and 15.4 k J mol^{-1}, respectively. The temperature evolution of the enthalpy for the metastable solid phase was investigated using previous measurements for the metastable solid phase: $T_{fus,m} = 219$ K and $\Delta H_{fus,m} = 9.8$ k J mol^{-1}.

The spontaneous evolution of the temperature of the undercooled liquid was followed from 188 K to 222.4 K under adiabatic conditions. This is interpreted in terms of phase transformations and kinetics. Three different processes can be considered. The first process leads to the quasi-complete transformation into the metastable solid phase from the undercooled liquid. Then the crystallization of the stable solid phase starts from the remaining undercooled liquid and further from the metastable solid phase. The third process corresponds to the melting of the metastable solid phase at 219 K and the rapid and simultaneous crystallization into the stable

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solid phase. At the end of the process, the complete transformation of the stable solid phase is observed.

1. Introduction

This study is part of an extensive work devoted to the study of the phase transformation kinetics and the glassy state in mixtures of hydrazine derivatives with water. We report here on methylhydrazine monohydrate ($CH_3NHNH_2 \cdot H_2O$, denoted as $MMH \cdot H_2O$) which appears as a defined compound in the phase diagram [1, 2].

Depending on the thermal treatment, this compound crystallizes in a metastable form which melts at about 219K and (or) in a stable one which melts at 234 K [3]. Previous studies by X-ray diffraction showed that the kinetics of the phase transformations are very slow and complex [4]. Cooling the liquid with rates as low as 0.1 K min^{-1} leads to a vitreous state avoiding any crystallization [4]. Real-time studies of the phase transformation kinetics are then possible. This aptitude to easy vitrification may be explained by the existence in the liquid of strong molecular associations due to the formation of hydrogen bonds [1, 2, 5].

We report here on the thermodynamic studies performed by adiabatic calorimetry. The heat capacities and enthalpies were measured from 100 to 265 K for the glassy state, the liquid, the undercooled liquid, and between 140 and 238 K for the stable solid phase.

The spontaneous evolution of the undercooled liquid temperature (enthalpy relaxation) under adiabatic conditions is discussed in order to get a better understanding of phase transformation kinetics and to evaluate the thermodynamic characteristics of the metastable solid phase.

2. Experimental

$MMH \cdot H_2O$ was supplied by the "Physico-Chimie Minérale II" team of the Pr. M. T. Cohen-Adad (Lyon I University). The methylhydrazine required to prepare the mixture was purified by distillation and kept under nitrogen. Water was deionized and degassed before use. The mixture was prepared by mass and the concentration checked by acidimetry or ultraviolet absorption spectrometry [1].

The adiabatic calorimeter used and its measuring system have been described previously [6]. The calorimeter vessel containing 3.19375g (0.049834 mol) was closed with an annealed gold gasket under a 1000 Pa pressure of helium. The first adiabatic shield is maintained at the same temperature as the sample. A platinum thermometer and a heating wire of constantan, within the vessel, enabled measurement of the temperature of the sample vessel before and after a heat input.

The temperature was measured with 0.0002 K precision. The precision of the heat measurement was about 0.02%. The cryostat was filled with liquid nitrogen and the

system was cooled to the lowest working temperature. The cooling time was shortened by admitting a few millimeters of dry helium. The cooling curve was recorded in order to get possible information about phase transitions. Enthalpy and heat capacity measurement were carried out on reheating from the lowest temperature. All calculations were made on an electronic desk computer.

3. Enthalpy and heat capacity measurements

3.1. Experimental conditions

The variation with temperature of the enthalpy $H(T)$ and the heat capacity $C_p(T)$ for MMH·H$_2$O on reheating are reported in Figs. 1a and 1b, respectively.

For all of these experiments, the sample was first cooled as fast as possible (≈ 2 K min^{-1}) from 300 to 100 K. This thermal treatment prevented any crystallization on cooling, thus leading to a glass at 100 K. The correction for the empty vessel contribution was applied. For enthalpy studies, the liquid state was taken as reference. This implies that the measured enthaly curves for all experiments were arbitrarily shifted for coincidence of the enthalpy curves for the liquid.

Three different experiments were further performed in order to measure the enthalpy and the heat capacity for the different phases (Figs. 1a and 1b).

The characteristics for the glassy state, the undercooled liquid and the liquid were deduced from two experiments. The first experiment was performed using a mean heating rate 0.13 K min^{-1} up to 238 K (above the melting of the stable solid phase). The enthalpy and the heat capacity curves (data drawn as • on Figs. 1a and 1b) may be divided into different regions limited by the points a, b, c, d$_1$, e, f, and g. The second experiment was performed with a smaller mean rate (0.04 K min^{-1}) up to 265 K. The enthalpy and the heat capacity curves (data drawn as ○ on Figs. 1a and 1b) may be also divided into different regions limited by the points a, b, c, d$_2$, e, f and g.

A third experiment was performed in order to study the stable solid phase behaviour. The glass was first reheated from 100 to 160 K. After several thermal cycles between 160 and 210 K, the sample crystallized in its stable solid phase which was then cooled to 140 K. Data (drawn as ▼ on Figs. 1a and 1b) were registered during reheating with a 0.1 K min^{-1} mean rate from 140 to 238 K. The important points on the corresponding curve are h, e, f and g.

3.2. Discussion

The (a, b) part of the curve corresponds to the enthalpy of the glassy state (Fig. 1a). The viscosity is very high and molecular movements are frozen. This glass is like a solid from the point of view rigid and elastic properties but has no three-dimensional periodicity. This means that the enthalpy slopes (Fig. 1a) and the heat capacity (Fig. 1b) for the glassy state and the stable solid phase are roughly identical in this region.
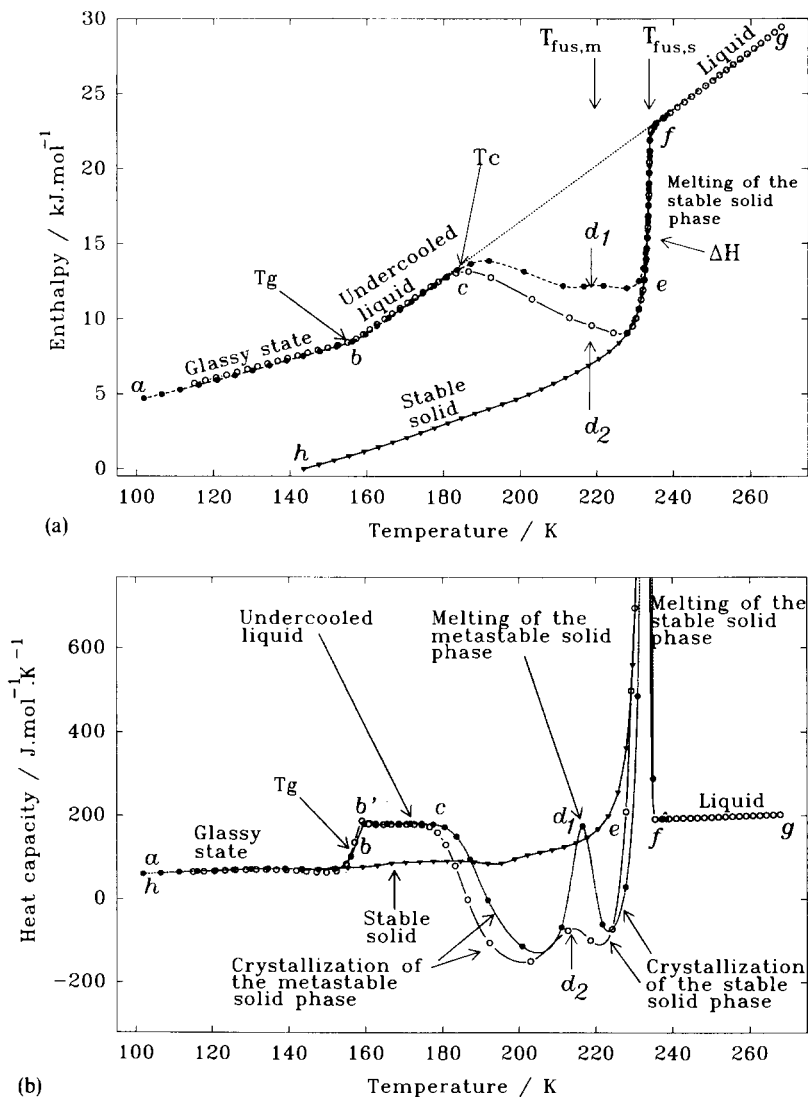
Fig. 1. Adiabatic calorimetry measurements for methylhydrazine monohydrate on reheating at: ●, 0.13 K min⁻¹ (after quenching); ○, 0.04 K min⁻¹ (after quenching); and ▼, 0.1 K min⁻¹ (only for the stable solid phase); (a) Enthalpy–temperature curves; (b) Heat capacity–temperature curves.

At the glass transition temperature (point b, Fig. 1b; $T_g = 157 \pm 1$ K), a sudden jump of the heat capacity ΔC_p was observed and was estimated to be 96.8 J mol⁻¹ K⁻¹. This was associated with a change of the enthalpy slope. The degrees of freedom are unlocked [7] and the glassy state transforms into an undercooled liquid whose thermodynamic characteristics are very similar to those of the liquid. As $C_{p,ul}$ and $C_{p,g}$ symbolize the heat capacity for the undercooled liquid (ul) and the glass (g),

respectively, the ratio $C_{p,\text{ul}}/C_{p,\text{g}}$ at T_g is estimated to be 2.2. Such a large increase in the heat capacity is usually observed in liquids without directional bonds. If we refer to Angell's classification, the glassy state of $MMH \cdot H_2O$ is extremely "fragile" compared with the "fragile" glass ethanol $(C_{p,\text{ul}}/C_{p,\text{g}} = 1.92)$ and to the "strong" $GeO_2(C_{p,\text{ul}}/C_{p,\text{g}} = 1.09)$ [8].

The slope of the enthalpy curve for the undercooled liquid ((b,c) line) is identical to that of the liquid ((f,g) line). This implies that the "structures" of these two liquids are similar despite the different values of the viscosity. At each temperature in the region (b,c) the undercooled liquid rapidly reaches a state of internal equilibrium but is nevertheless thermodynamically metastable compared with the solid state.

Between about 180 and 233 K (curves represented by the points c, d_1 (or d_2), e and f), the enthalpy and the heat capacity variations are more complex. Their decreasing denotes cyrstallization processes. This confirms previous studies showing that the crystallization of a metastable and/or a stable solid phase(s) may occur from 180 to 228 K after a nucleation during extended annealing near T_g (optimum temperature domain from 155 to 165 K) [4].

The undercooled liquid crystallizes first into the metastable solid phase followed by a second crystallization into the stable solid phase.

During reheating at 0.13 K min^{-1}, the heat capacity exhibits an endothermic anomaly (point d_1) at about 219 K which corresponds to the melting of the metastable solid phase. This melting is not so clearly observed during reheating at a slower rate (0.04 K min^{-1}, point d_2). According to previous results [4], this proves that the transformation to the stable solid phase from the metastable solid one is more complete than during the first, quicker, experiment. The quantity of metastable solid to melt is then lower.

The h to e region is characteristic of the stable solid phase where the enthalpy and the heat capacity roughly present linear variations in a large temperature domain. The stable solid phase melts at 234 K. The melting enthalpy was estimated to be 15.4 kJ mol^{-1} which confirms previous measurements [1].

In the f to g region, the enthalpy and the heat capacity of the liquid phase present linear variations.

4. Kinetics of phase transformations: spontaneous evolution of the system under adiabatic conditions

4.1. Experimental procedure

Previous differential scanning calorimetry (DSC) experiments showed a complex overlap of the crystallization processes of the metastable and the stable solid phases and their kinetics [4]. By adiabatic calorimetry, reheating at rates of 0.13 or 0.04 K min^{-1} is still too rapid for clear separation of the melting of the metastable solid phase and the crystallization into the stable solid phase. Furthermore, due to the slowness of these processes, they cannot be studied by dsc under isothermal conditions. The heat effects become too small to measure with confidence.

To get a better understanding of these processes, the spontaneous evolution of the undercooled liquid was studied under adiabatic conditions. The system (sample vessel) was first rapidly cooled (1.3 K min^{-1}) from 300 K to 140 K (under T_g 157 K) and then reheated from 140 to 158 K. During 13 h annealing at 158 K, no significant evolution of the system was observed. The system was then "rapidly" reheated ($\approx$ 2 K min^{-1}) to 186 K from where the spontaneous evolution of the system's temperature was followed for 13 h under adiabatic conditions. Because of a transient period the temperature variation was accurately measured from $T_0 = 188$ K.

4.2. Analysis of the results

On cooling, no crystallization occurs. The nucleation of the two solid phases is favoured by annealing for 13 h at 158 K. This process involves so little fraction of compound that no temperature change is observed.

After reheating to 186 K and stabilizing under adiabatic conditions the undercooled liquid restores its excess energy to the system and the temperature increases to 222.4 K. The variation of the temperature with time is reported in Fig. 2 and exhibits a more or less fast and complex behaviour which depends on the rate and the overlap of the two crystallizations.

The temperature rate dT/dt was then calculated from the experimental data.

The enthalpy curves for the stable solid phase, the undercooled liquid and the liquid are reported in Fig. 3. The dT/dt curve, symbolized by ▲, is also drawn on the same figure according to the following principles:

(1) The enthalpy of the system at the beginning of the experiment (188 K) is given by the point A situated on the extrapolated line of the enthalpy curve for the undercooled liquid.
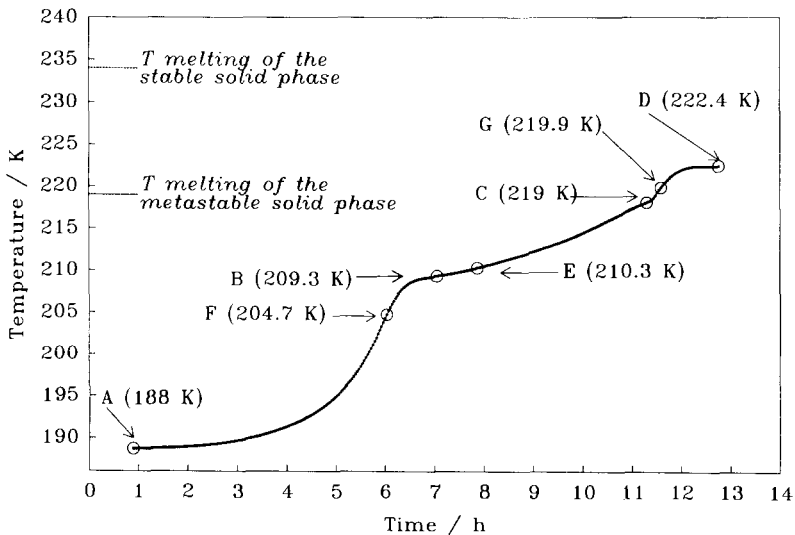
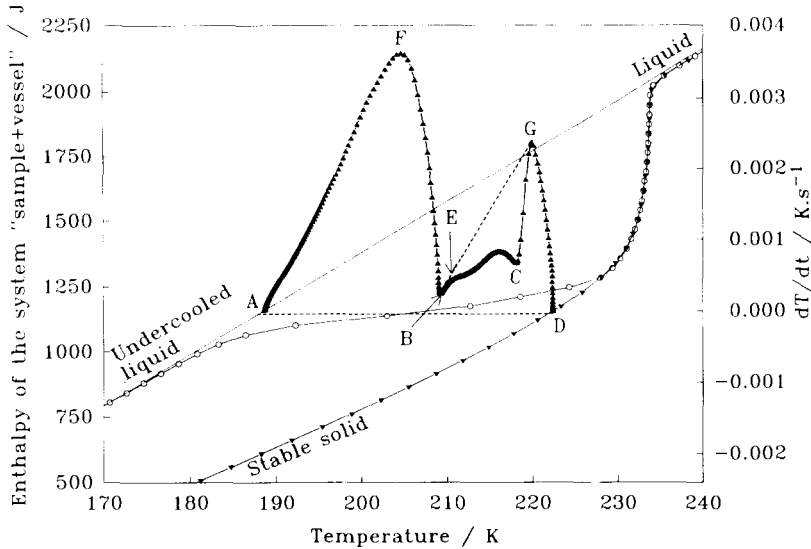Fig. 2. Time evolution of the temperature of the system under adiabatic conditions.

Fig. 3. Enthalpy–temperature curves of the system (sample vessel) on reheating at: ●, 0.04 K min⁻¹ (after quenching), ▼, 0.1 K min⁻¹ (only for the stable solid phase); ▲, Variation of dT/dt with temperature.

(2) According to the adiabatic conditions the enthalpy of the system (sample + vessel) remains constant during the process and is represented by the horizontal dotted line starting from point A to point D. The crystallization process is finished at the point D where the temperature remains constant ($T = 222.4$ K, dT/d$t = 0$).

The variation of dT/dt with temperature may be divided into three different parts:

(1) Between 188 and 204.8 K (from A to F), dT/dt (T) exhibits a quasi-linear increase which corresponds to the transformation of the undercooled liquid into the metastable solid phase [4].

(2) From 204.8 to 209.3 K (from F to B), dT/dt (T) decreases rapidly to a non-zero value. At 209.3 K, the crystallization into the metastable solid phase from the undercooled liquid is finished.

(3) Between 209.3 and 222.4 K (from B to D), dT/dt (T) exhibits a more complex variation:

From B (209.3 K) to E (210.3 K), it seems to be quasi-linear with a slope roughly equal to that observed during the crystallization of the metastable solid phase (AF curve). This probably indicates a new single process of the transformation with equivalent kinetics. This process starts before the end of the crystallization of the metastable solid phase. It may be interpreted as the rapid and complete crystallization of the stable solid phase from the remaining undercooled liquid.

From E (210.3 K) to C (218.1 K), dT/dt (T) shows a more complex and much slower variation. This may be interpreted as the solid–solid transformation of the metastable solid phase to the stable solid one.

Between C (218.1 K) and G (219.9 K), the untransformed metastable solid domains melt. The metastable liquid obtained crystallizes into the stable solid phase rapidly and quasi-simultaneously. The melting temperature of the metastable solid phase $T_{\mathrm{fus,m}}$ is estimated to be 219 K which confirms previous measurements [1, 4].

Between G (219.9 K) and D (222.4 K), dT/dt (T) decreases abruptly to zero. At 222.4 K, the enthalpy of the system is equal to that of the system when the compound is in its stable phase. This indicates the end of the complete transformation into the stable solid phase. The system has reached a stable equilibrium state after spontaneous evolution for 13 h.

Remark: For various starting temperatures, drawing horizontal lines (such as (AD)) in Fig. 3 should enable prediction of the final equilibrium temperature and the compound state. For example, starting the experiment at 175 K will lead to a final temperature of 207 K which is lower than the melting temperature of the metastable solid phase. This experiment was undertaken but stopped after 24 h as the evolution of the system was too slow.

Because of the complexity and the overlapping of the phase transformations, a mathematical simulation of these processes is not easy. This study is now in progress.

4.3. Enthalpy–temperature curve of the metastable solid phase

The variation of the molar enthalpy with temperature for the metastable solid phase, denoted $h_{\mathrm{m}}(T)$, is determined assuming that:

(1) The melting enthalpy of the metastable solid phase at 219 K, estimated to be 9.8 kJ mol^{-1} from previous studies [1], corresponds to a complete transformation. This assumption leads to the point K (Fig. 4) belonging to the $h_{\mathrm{m}}(T)$ line.

(2) The variation of the enthalpy versus temperature is linear up to the melting temperature.

(3) The slope of $h_{\mathrm{m}}(T)$ is roughly equal to that of the stable solid phase.

The variation of $h_{\mathrm{m}}(T)$ has been reported in Fig. 4 in the temperature domain 175–219 K. The analysis of the enthalpy curves of the metastable solid phase $h_{\mathrm{m}}(T)$ and the sample without vessel $h_{\mathrm{c}}(T)$ enable estimation of the untransformed fraction just before the beginning of the transformation into the stable solid phase.

The variation of the enthalpy for the sample (without vessel) was first determined. If $H_{\mathrm{V}}(T)$ is the enthalpy of the vessel and K the constant enthalpy of the system (sample + vessel), the enthalpy $H_{\mathrm{c}}(T)$ of the sample ($m = 3.19375$ g) is simply given by:

$$H_{\mathrm{c}}(T) = K - H_{\mathrm{V}}(T)\,(\mathrm{J}) \qquad (1)$$

The variation of the molar enthalpy of the sample $h_{\mathrm{c}}(T)$ is deduced from the known heat capacity of the vessel and the molar enthalpy of the undercooled liquid $h_{\mathrm{ul}}(T)$ at 188 K leading to:

$$h_{\mathrm{c}}(T) = -201.1\,T + 52098.7\ (\mathrm{J\,mol}^{-1}) \qquad (2)$$
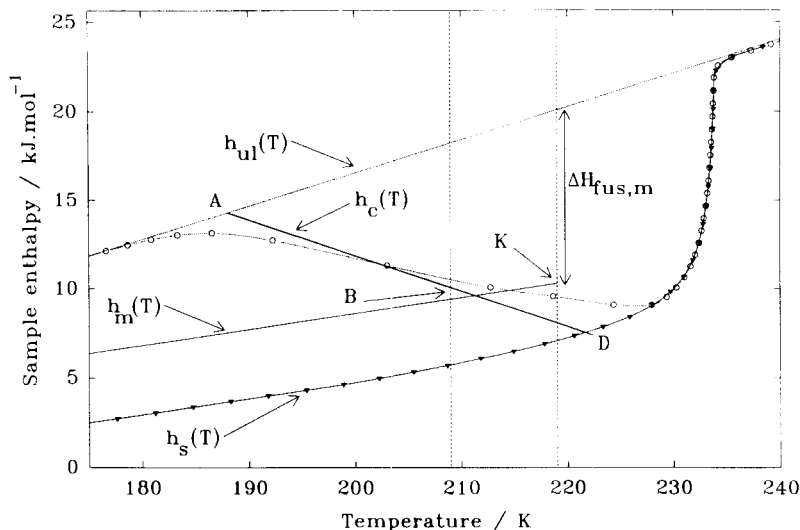
Fig. 4. Enthalpy–temperature curves of the sample for different phases on reheating at: ○, 0.04 K min⁻¹ (after quenching) and ▼, 0.1 K min⁻¹ (only for the stable solid phase); $h_{fus,m}(T)$ symbolizes the estimate of the enthalpy for the metastable solid phase. The line AD characterizes the enthalpy relaxation of the sample during the adiabatic experiment.

The variation of $h_c(T)$ is reported in Fig. 4 from the point A (188 K) to the point D (222.4 K) where the relaxation process is finished. The molar enthalpy curves for the stable solid phase $h_s(T)$ (drawn as ▼) at 0.1 K min⁻¹ and for the undercooled liquid $h_{ul}(T)$ (drawn as ○) during reheating at 0.04 K min⁻¹ are also recalled. At the end of the crystallization processes (point D) the enthalpy of the sample is about 7.4 kJ mol⁻¹ which is almost equal to that of the stable solid phase, 7.2 kJ mol⁻¹. This proves the complete crystallization into the stable solid phase.

Assuming that the mixing enthalpy, particularly at the end of the transformation (209 K), is weak compared to $h_c(T)$ and $h_m(T)$, the fraction of the metastable solid domains, denoted x, may be expressed by:

$$h_c(T) = xh_m(T) + (1-x)h_{ul}(T) \tag{3}$$

where $h_{ul}(T)$ is the molar enthalpy for the undercooled liquid. The value of x is then easily determined from Fig. 4. At 209 K (point B), the untransformed fraction is estimated to be about 0.10 showing that the transformation of the undercooled liquid to the metastable solid phase is quasi-complete.

5. Conclusions

The enthalpy and the heat capacity of the defined compound MMH·H₂O has been measured in the liquid, the undercooled liquid, the vitreous state and the stable solid phase.

On reheating, after rapid cooling at low temperature, the compound exhibits a glass transition ($T_g \approx 157$ K) with an important heat capacity jump ($\Delta C_p = 96.8$ J mol^{-1} K^{-1}). The glassy state belongs to the extremely "fragile" class defined by Angell. Studies of the glassy state behaviour are now in progress.

Studying the crystallization processes for the metastabe and the stable solid phases is not easy because of slowness, complexity and overlapping of the exo- and endothermic events. Spontaneous evolution of the system is observed at 188 K under adiabatic conditions. The first process leads to the quasi-complete transformation into the metastable solid phase from the undercooled liquid with relatively simple kinetics. The complex crystallization of the stable solid phase starts from the remaining undercooled liquid and further from the metastable solid phase. The third process leads to the melting of the metastable solid phase and then the quick growth of the stable solid phase.

Particular attention will be further given to analysis of this competition between the melting of the metastable solid phase and the simultaneous crystallization of the stable solid phase. Mathematical simulations are now in progress.

The melting temperature $T_{fus,s}$ and the melting enthalpy $\Delta H_{fus,s}$ for the stable solid phase have been estimated to be 234 K and 15.4 kJ mol^{-1} and agree well with previous studies. In accordance with previous experiments, the temperature evolution of the enthalpy for the metastable solid phase has been investigated and quasi-complete crystallization of the metastable solid phase from the undercooled liquid was observed.

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