

# Analysis of Modelling Capabilities of Phase Transitions of the First Kind in Hydrated Sodium Acetate

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**Abstract** – The phenomenon of phase transitions of the first kind is explained on the example of hydrated sodium acetate  $\text{CH}_3\text{COOHNa}$ , which in room temperature is a solid body, and after exceeding the phase transition temperature of  $T_{\text{PF}} \cong 330 \text{ K}$  ( $57^\circ\text{C}$ ), it turns into a liquid. The substance, when in a liquid state, characterizes with its ability to change into a supercooling state, until it reaches the temperature nearing  $0^\circ\text{C}$ . It is possible to initiate the process of a phase transition while  $\text{CH}_3\text{COOHNa}$  is in the state of undercooling ( $0^\circ\text{C} \leq T \leq 57^\circ\text{C}$ ) by switching on an acoustic generator (20 kHz). The acoustic signal which initiates the phase transition (in the state of  $\text{CH}_3\text{COOHNa}$  undercooling) may also be generated in a different manner, for example through bending a properly profiled metal plate which will be inserted inside the sample. The phase transition that has been initiated in this way can be observed through crystallizing the substance, which was used as a specimen; and it indicates a phase transition of the first kind, during which huge amounts of latent heat are released. Therefore the occurring amorphous substance transition is an exothermic process.

**Keywords:** Phase transitions, Hydrate sodium acetate, Thermal properties, Latent heat.

## 1. Introduction

Hydrated sodium acetate has been increasingly used for the accumulation of heat energy in heating systems based upon, among others, the buffer system (Web t– 1). The greatest benefit of employing this chemical is, by far, a larger thermal capacity per mass unit of the substance, accumulated within the temperature range of  $55\text{--}60^\circ\text{C}$ , compared to traditionally used water. When we use mixtures of hydrated sodium acetate together with additives that are meant to improve thermal conductivity as well as a life span, it is possible to design an environmentally friendly source of energy, accumulated in a particular mixture and possible to obtain from the energy of phase transitions of the first kind according to Ehrenfest classification of phase transitions, that is a change in a state of matter from liquid into a solid body. This article shows determining phase transition energy through experiments (for pure hydrated sodium acetate, this value equals approximately  $260 \text{ kJ/kg}$  (Green, 1908; Keinänen, 2007)) on 90% hydrated sodium acetate, which serves as an example, alongside with a numerical analysis of a given issue.

## 2. Laboratory Stand and Object of Study

The examined samples, (look at Fig.1 – example of hydrated sodium acetate) are heated in boiling water for 10 min. and then cooled down to room temperature. The internal structure of the sample is

undercooled liquid (which was formed through the melting of a crystallized solution). Fig. 2 illustrates thermal history of preparing the sample for the sake of the examination.



Fig. 1. Tested sample (prior to measurement – liquid in a PVC soft bag; on completion of the measurement – solid body in PVC; hydrated sodium acetate).

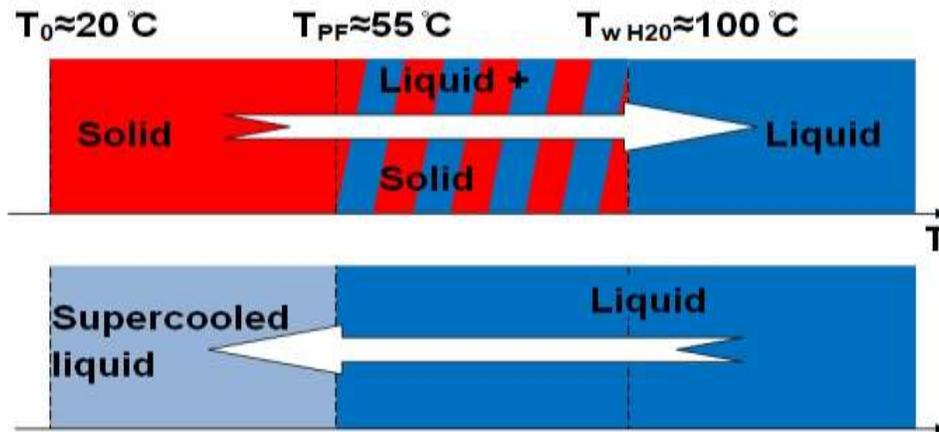


Fig. 2 Thermal history of preparing the samples for testing.

In order to determine the temperature of phase transition, it is necessary to use a sample that had been prepared for examination during a previous stage and measure the temperature on the surface of the sample through a type K thermocouple, as shown in Fig.3. In addition we show a simple measuring set-up as well as a method of specifying the temperature  $T_{PF}$ . The temperatures of phase transition for sodium acetate can be found in literature (Green, 1908; Watson, 1973), equalling approximately  $58\text{ }^{\circ}\text{C}$ .

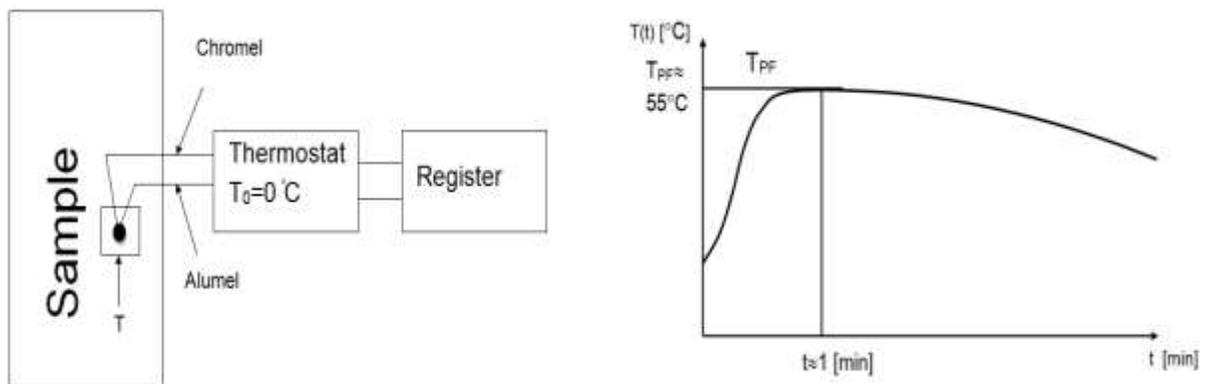


Fig.3 Block diagram of a stand and a method of determining temperature  $T_{PF}$ .

After ensuring the electrical connections have been properly joined and also the thermostating temperature has levelled to  $T_0 = 0\text{ }^{\circ}\text{C}$  on the cold tips of the thermocouple, the measurement of the changes in the thermoelectrical power  $E(t) = k \cdot [T(t) - T_0]$  is released by means of an acoustic signal (bending of a metal plate in the sample). The approximate time of making the measurement in temperature changes on the surface of the examined sample lasts about 1 minute.

### 3. Method of Determining Latent Heat of Phase Transition

The heat of a phase transition  $L_{PF}$  is calculated on the assumption that we know temperature characteristics both in specific heat changes of the examined substance in its solid state as well as in the supercooled liquid phase  $c_L$ . The required heat value of the phase transition  $L_{PF}$  of the sample material in question is calculated on the basis of a thermal balance of a thermodynamic system (Raznjevic, 1966). Moreover, it is assumed that:

- The thermodynamic system depicted in Fig. 4 is an adiabatic system;
- The mass  $m_{H_2O}$  and the initial temperature of water  $T_{0,H_2O}$  in the adiabatic system are known prior to the insertion of the examined sample;
- We know the mass  $m$  and the initial temperature  $T_0$  of the substance which forms the sample, whose phase transition heat  $L_{PF}$  must be determined, with  $T_{0,H_2O} < T_{PF}$ ;
- The phase transition of the examined substance begins when locally, due to fluctation, the temperature  $T_{PF}$  has been reached (transformation of an acoustic wave into heat), and then the front of  $T_{PF}$  temperature moves inwards the sample.
- After initiating a phase transition in the sample's material, it is placed in a measuring set-up (Fig. 4); next, changes in water temperature begin to be registered until thermodynamic equilibrium has been reached, which corresponds to equal temperatures of all components of the thermodynamic system, and equals  $T_K$ ; at the same time, for even distribution of water temperature, we move the measuring set-up, thus stimulating an introduction of a dynamic heat transfer, cyclically every 15 sec.

Taking into account the above-mentioned assumptions, heat balance is calculated, where on determining  $L_{PF}$  in the first approximation, only water and the sample material are considered; see below:  
The heat lost by a substance which forms the sample material:

$$Q = mL_{PF} - mc_L \int_{T_0}^{T_{PF}} (T_{PF} - T_0) + mc_S \int_{T_0}^{T_{PF}} (T_{PF} - T_K) \quad (1)$$

In the above equation:

- The first part  $mL_{PF}$  stands for heat which is given off by the examined substance due to a phase transition;
- The second part  $mc_L \int_{T_0}^{T_{PF}} (T_{PF} - T_0)$  stands for heat absorbed from the set-up by the examined substance, so that the temperature  $T_{PF}$  of the phase transition could be reached;
- The third part  $mc_S \int_{T_0}^{T_{PF}} (T_{PF} - T_K)$  is heat given off by the sample material after its cooling down from  $T_{PF}$  to the final temperature  $T_K$  (thermodynamic equilibrium).

The heat gained by water in a calorimeter as well as PVC and PP:

$$Q_{PF} = m_{H_2O} c_{H_2O} \int_{T_{0,H_2O}}^{T_K} (T_K - T_{0,H_2O}) + m_{PP} c_{PP} \int_{T_0}^{T_K} (T_K - T_{0,PP}) + m_{PVC} c_{PVC} \int_{T_0}^{T_K} (T_K - T_{0,PVC}) \quad (2)$$

- The component  $m_{PVC} c_{PVC} \int_{T_0}^{T_K} (T_K - T_{0,PVC})$  refers to the heat absorbed by the material, where there is a specimen (soft PCV), so as to obtain temperature  $T_K$  (of the thermodynamic equilibrium)

- The component  $m_{PP}c_{PP}|_{T_0}^{T_K}(T_K - T_{0,PP})$  refers to the heat absorbed by the material, where there is a specimen with water (polipropylene-PP) so as to obtain temperature  $T_K$  (of the thermodynamic equilibrium).

When comparing the two expressions (1) and (2), it is assumed that the heat  $L_{PF}$  of the phase transition of hydrated sodium acetate equals:

$$L_{PF} = \frac{m_{H_2O}}{m} c_{H_2O} |_{T_{0,H_2O}}^{T_K} (T_K - T_{0,H_2O}) + c_L |_{T_0}^{T_{PF}} (T_{PF} - T_0) - c_S |_{T_0}^{T_{PF}} (T_{PF} - T_K) + \frac{m_{PP}}{m} c_{PP} |_{T_0}^{T_K} (T_K - T_{0,PP}) + \frac{m_{PVC}}{m} c_{PVC} |_{T_0}^{T_K} (T_K - T_{0,PVC}) \quad (3)$$

#### 4. Modelling the Elements of the Measuring Set-up

The numerical calculations were made in the COM SOL 3.5a environment by COM SOL MULTIPHYSICS company. The analyses employed the Heat Transfer Module (COMSOL Multiphysics 2010), the geometry and the grid of the model in question (illustrated in Fig. 4), which also shows a simplified model of the actual set-up, alongside with the descriptions of particular elements.

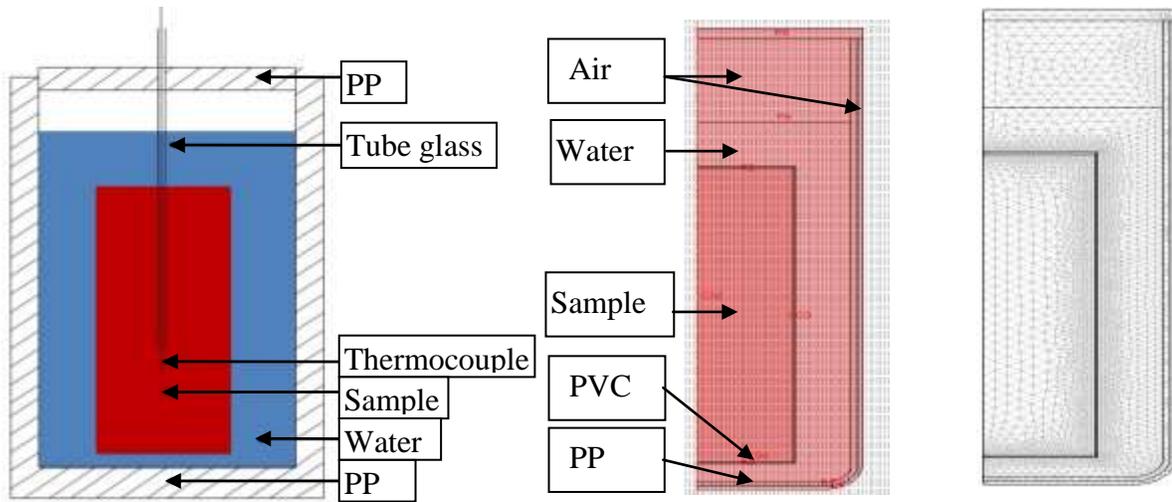


Fig.4. Simplified set-up of placing the sample on a laboratory stand for the examination of phase transfer heat of the first kind, and a geometrical model which underwent simulation together with the calculation grid for a given model.

In the numerical model we introduced simplifying assumptions, as below:

- We introduced axi-symmetrical two-dimensional geometry while maintaining equal volume of the examined sample (the real sample is not cylindrical);
- The dynamism of heat transfer through moving the water in the vacuum flask was replaced by a replacement parameter of water thermal conductivity ( $k=600 \text{ W/m}^1\text{K}^{-1}$ ), which models uniform distribution of water temperature;
- The model is deprived of measurement elements in the form of a thermocouple and a glass pipe, which leads up the thermocouple to the sample;
- The temperature distribution in the numerical sample as well as in the water is taken from the same two points throughout the examination, which may not happen in reality;
- The model sample is stationary and positioned centrally, which is also a simplification, eliminating the sample's movement during the measurements;
- The parameters of the sample in the model have been introduced as values independent of the temperature (parameters = constant).

The thermophysical properties of the numerical module elements have been assumed accordingly to the set-up of the real one, as shown in Fig. 4, available in literature; see the table of value listings below (Tab. 1).

Table 1. Thermophysical properties of numerical module elements (Keinänen, 2007; Raznjević, 1966; Titov, 1984; Web – 2).

Lp.	Elements of numerical model (materials)	Thermal conductivity [ $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ]	Density [ $\text{kg}\cdot\text{m}^{-3}$ ]	Heat capacity [ $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ ]
1	Hydrated sodium acetate	0.6	1400	2850
2	Water	0.597 (600*)	998	4180
3	PVC (polyvinyl chloride)	0.159	1250	1800
3	PP (polypropylen)	0.16	900	1700
5	Air	0.025	1.18	1005

\*replacement parametre due to an introduction of a dynamic heat transfer in water

## 5. Results of Analysis

The values of temperature rise in water, experimental and those resulting from the numerical analysis, have been introduced in Fig. 5, where during the first thirty minutes, measurements of water temperature were made in thirty-second time intervals, and at the end of the measurements, 40 minutes after beginning the experiment. Therefore, it may be stated that the selected model comes very close to the course of the process of temperature levelling of the real pattern. We have presented two characteristics of temperature change, inside the examined sample of hydrated sodium acetate ( $r = 18$  mm) and in the water ( $r = 20$  mm). The measurements of temperature field for the presented numerical model prove that as for the difference in temperatures in the sample with water temperature (where the sample had been placed), by the end of the simulated process (after 40 min.), the difference in temperature between the tested objects equals approximately  $1^\circ\text{C}$ .

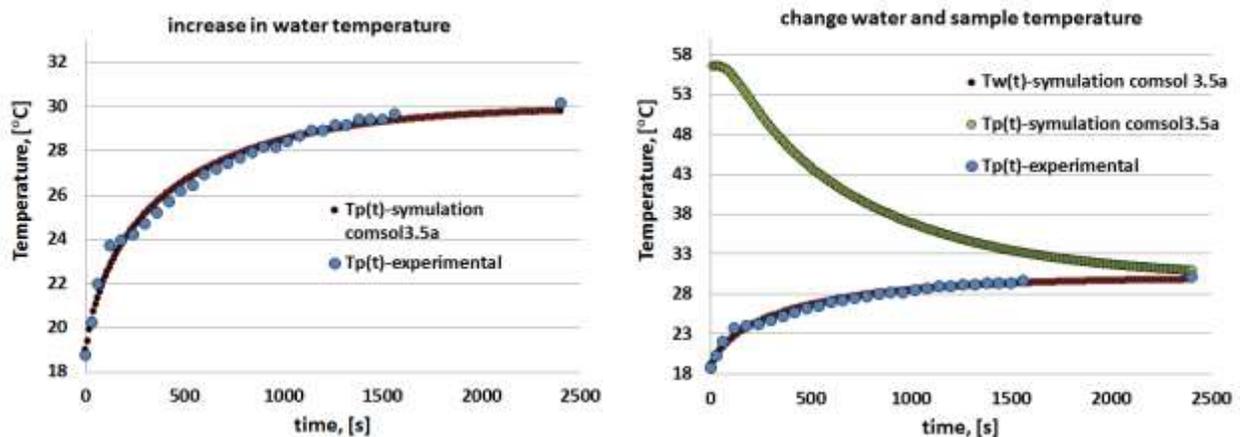


Fig.5. Temperature change in water and the examined sample (simulation and experimental).

We also present a graphic distribution of temperature field for the examined material, where we simulated an introduction of phase transfer heat, with  $t = 2400$  s (Fig. 6), both for the model with static as well as dynamic latent heat transfer (we introduced a replacement co-efficient of thermal conductivity). The measurement values of phase transition energy in its initial stage of sample temperature that were determined for experimental research have been illustrated in Fig. 6. The red point on this diagram refers to the latent heat value of phase transition, obtained through analytical calculations and which enabled to conduct a numerical simulation. The value calculated in this simulation is represented by a black point.

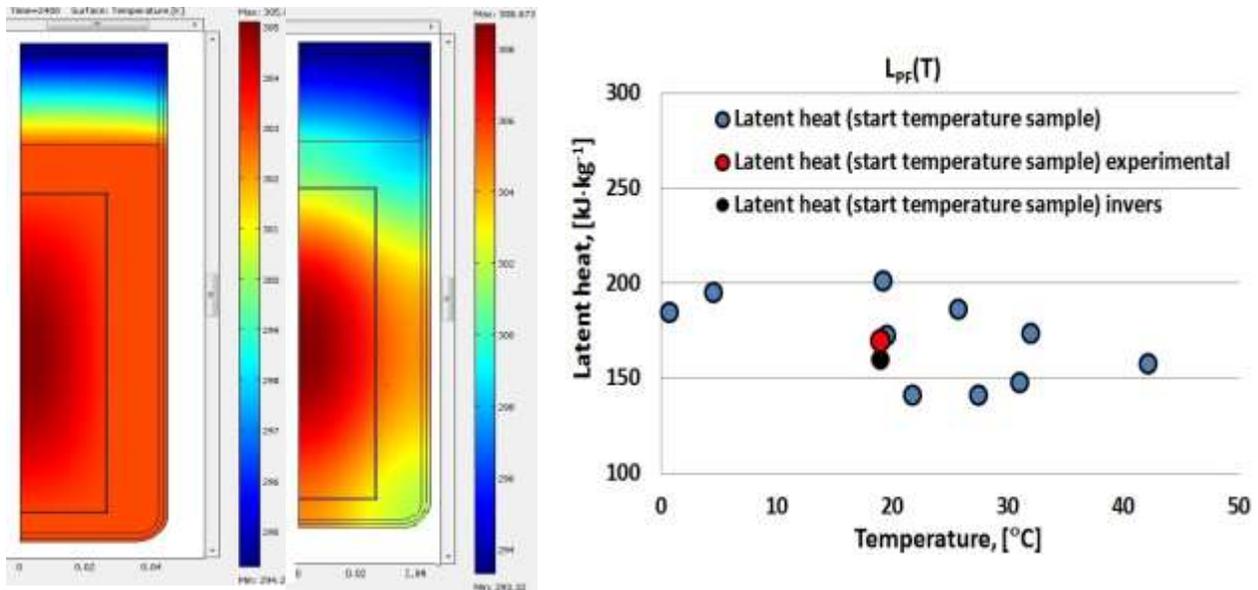


Fig.6. Temperature field in the modelled set-up, and energy values of the phase transition in the function of initial temperature of the examined sample.

## 6. Conclusion

The study presents comparative results of a numerical analysis versus a real measurement, as a result of the initiated process of latent heat transfer from the energy of phase transition (we simulated a static and a dynamic model of heat transfer between the sample and the water). While evaluating the above analysis, it is essential to remember that we introduced simplifying assumptions which enabled us to perform the analysis of determining latent heat phase transition of the examined substance. Moreover we presented experimental calculations of the energy of phase transition, depending upon the initial temperature of the examined sample. The difference between the obtained heat values of the phase transition results, among others, from too short intervals between particular tests, which might have had a negative effect on heat balance in a given set-up. In addition, some measurements were conducted during cooling down of the examined samples to the temperature of approximately  $1^{\circ}\text{C}$ , which considerably affected the changing value of specific heat in the examined substance in the form of a liquid (specific heat changes in the temperature function); in the calculations we assumed a constant value. We did not take into consideration variable values of thermophysical parameters for particular elements of the measuring set-up, either. Theoretical heat of phase transition for sodium acetate equals approximately  $260 \text{ kJ/kg}$  (Hiegel, 1980; Keinänen, 2007), whereas for hydrated sodium acetate which is present in the examined sample (sodium acetate with approximately 15% water content) equals approximately  $145 \pm 10 \text{ kJ/kg}$  (assessed value) (Keinänen, 2007). The above-mentioned research analysis leads to a conclusion that the prepared numerical model has 5% accuracy in mapping the experimental course of the research. During a further stage of the study, one may attempt to perfect the measuring set-up through automatic archiving of data and reading particular temperatures of both water as well as the surface and side of polyvinylchloride (PP), by using automatic schemes. It is also possible to improve the dynamics of heat transfer among particular objects (water – sample).

## References

- Blumm J., Lindermann A. (2003/2007) High Temperatures – High Pressures, v35/36.  
 COMSOL Multiphysics User's Guide Version 3.5a, (2008).  
 Green W. F. (1908) The "melting-point" of hydrated sodium acetate: solubility curves, J. Phys. Chem., 12, pp.655-660.  
 Hiegel G. A. (1980): Crystallization of sodium acetate, J. Chem. Educ., 57 (2), pp 152.

Keinänen M. ( 2007): Latent heat recovery from supercooled sodium acetate trihydrate using a brush heat exchanger, Helsinki University of Technology, Espoo, pp 14-16.  
Raznjević K. ( 1966): Tablice Cieplne z Wykresami WNT, Warszawa.  
Watson W.K.R. ( 1973): Heat transfer system employing supercooled fluids. United States Patent 3952519. P. 9. San Diego.  
Wiśniewski S. ( 2009): Termodynamika Techniczna , WNT, Warszawa.  
Titow W. V. (1984): PVC Technology Elsevier, fourth edition, Applied Science Publisher, pp 1186.

Websites:

Web- 1 : [http://www.luxheizung.pl/userfiles/image/Karty\\_PDF/informacje\\_techiczne-PCMX.pdf](http://www.luxheizung.pl/userfiles/image/Karty_PDF/informacje_techiczne-PCMX.pdf) 20 January 2014.  
Web - 2 : [http://www.segerfrojd.com/thermal\\_properties.htm](http://www.segerfrojd.com/thermal_properties.htm) 20 January 2014