

# *Study on the Relationship Between Specific Heat Capacity and Temperature of Unary Molten Salt*

Zhencheng Lu<sup>1</sup>, Qingguo Zhao<sup>1</sup> and Yuting Wu<sup>1,a,\*</sup>

<sup>1</sup>Key Laboratory of Enhanced Heat Transfer and Energy Conservation, Ministry of Education and Key Laboratory of Heat Transfer and Energy Conversion, Beijing Municipality, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China  
a. s201805114@emails.bjut.edu.cn

\*corresponding author: Yuting Wu

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**Abstract:** The specific heat capacity data of unary salt measured by different experimenters have certain differences due to the different experimental conditions. This paper focuses on the study of differential scanning calorimetry for measuring the specific heat capacity of molten salt. The data measured by different experimenters will be analyzed and compared, and finally more reasonable data will be screened out. The results show that in the molten state, the specific heat of NaNO<sub>3</sub>, KNO<sub>3</sub>, and LiNO<sub>3</sub> is almost constant. Part of the reason for the difference in the experimental values of the specific heat capacity of different experimenters is that the temperature range of the solid-liquid coexistence zone is not consistent. The filtered data of this paper can be used as the basis for predicting the specific heat capacity of the mixed molten salt.

## 1. Introduction

Molten salt is a melt of inorganic salt. It has a wide temperature range, large heat capacity, good thermal stability, large thermal conductivity, low viscosity, good fluidity, low vapor pressure, high relative density, low cost and good compatibility with metal materials. Compatibility and other advantages[1] are widely used as the material of choice for heat transfer and storage media.

The thermophysical parameters of molten salt are the basic data for the design and calculation of molten salt heat storage system, and are also the main basis for formulating and screening molten salt formulations with excellent heat transfer and heat storage. In the design of heat transfer and storage systems, the specific heat capacity is one of the most important parameters. The influence of specific heat capacity on the heat transfer and storage system is reflected in the size of the stored heat energy, which affects the design of the system capacity.

Over the years, increasing experimenters have carried out a lot of research in order to be able to find better properties of molten salt. Among them, the specific heat capacity of molten salt, a thermophysical property, will be affected by different experimental conditions and different experimental measurement methods. There will be a certain difference in the specific heat capacity of the same molten salt.

Molten salts generally include chlorides, fluorides, carbonates and nitrates, among which nitrates are widely used as heat transfer and storage media in solar power stations because of their low melting point and high thermal stability below 500°C[2-6]. This article will study the experimental method of measuring the specific heat capacity of molten salt, and mainly focus on nitrate, which is commonly used as the heat transfer and storage medium in solar power stations. The specific heat capacity values measured by different experimenters are analyzed and compared, and some reliable specific heat capacity experimental data can be summarized through the error analysis of the experimental method.

## 2. Research on Experimental Methods

There are two methods for measuring specific heat capacity: one is Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA). DSC and DTA have the same principles and are similar, but the performance of DSC is better than that of DTA. It is more accurate than DTA, and has better resolution and reproducibility than DTA. The reason is that DTA measures the temperature difference between the sample and the reference simultaneously, while DSC measures the power difference between the sample and the reference. DSC measures the temperature difference error smaller. In the past few decades, the development of differential scanning calorimetry has evolved from a semi-quantitative DTA method to a true calorimetry[7].

The most widely used method for measuring specific heat parameters in modern times. In the 1960s, in order to overcome the shortcomings of differential thermal analysis technology that is difficult to carry out quantitative analysis, differential scanning calorimetry analysis technology was developed and applied on its basis. Differential scanning calorimetry is a measurement technique that measures the relationship between the energy difference input to the sample and the reference substance and the temperature (or time) under the program control temperature[8].

Common calibration problems of DSC: When measuring the specific heat capacity, different calibration coefficients should be used for the measurement of the specific heat capacity in the transition region of the phase change and the measurement of the specific heat capacity in the solid or liquid state. It can be expected that the calibration factor of the heat flow rate depends on the specific heat capacity of the heat flow rate itself. For different types of DSC, the uncertainty of heat capacity measurement is usually between 5% and 20%, and for power compensation DSC, it is between 3% and 5%. Higher accuracy requires a lot of time and effort to perform correct calibration. Only by ensuring the same conditions as possible (equal mass, equal thermal conductivity, equal heating range, equal specific heat capacity) during the calibration run and the measurement run can all potential sources of system error remain constant. Only these conditions are met Under the conditions, the use of DSC for specific heat measurement can ensure accuracy. At the same time, please refer to SabbahR[9] for the selection of reference materials.

Common error analysis of DSC: (1) The analysis of GWHHöhne[11] shows that when measuring the specific heat capacity by DSC method, the temperature range of the sampling point is too low, which will cause the measurement result of the specific heat to be lower. The appropriate temperature range can reduce this Influence (approximately the best temperature range is 5K-10K). (2) It shows that when using the DSC method to measure the specific heat capacity, it is necessary to use two independent furnaces to heat the sample and the reference. The furnace used as a reference does not contain the sample, so the two systems are The heat transfer conditions are not the same, resulting in irreparable heat loss and dynamic measurement errors. PoeBneckerW [10] analysis shows that the dynamic measurement error can be determined by measuring the loss before scanning mode and after isothermal mode. (3) The analysis of GWHHöhne[11] shows that when the specific heat capacity is measured by the DSC method, at a temperature higher than 20°C, the heat

flow rate of the machine will be strongly interfered and tampered with at the beginning of the work, which will affect the measurement result of the specific heat capacity. change.

General precautions to minimize the error and error estimation[11-15]: Differential scanning calorimetry measurement of specific heat capacity will have at least 1%-5% error. To obtain a more reliable specific heat capacity value, it is necessary to know the true heat flow rate entering the sample (that is, the difference between the recorded signal and the zero line). Under normal circumstances, some hidden heat transfer conditions unavoidable changes will cause errors in the measurement of specific heat capacity. In order to minimize the errors caused in daily experimental operations, the following measures should be taken:

(1) The room temperature of the experimental environment must be kept constant during the experiment.

(2) The sample and reference material should have similar heat capacity and should have similar thermal conductivity as best as possible.

(3) This must be kept in mind when choosing an appropriate temperature interval. The temperature interval of a single operation shall not exceed 100 to 200K. If a larger temperature range is required, it should be divided into appropriate sub-intervals. For DSC in a constant temperature environment, in principle, the isotherm and the starting isotherm are nonlinearly connected (due to the asymmetry of radiation and convection losses), and this trend will increase at higher temperatures. Performing multiple measurements at the same temperature interval helps to detect the possible differences in the observed specific heat capacity, thereby reflecting the uncertainty of the experiment.

(4) The heating and cooling operation should be performed and compared during the measurement.

(5) The measurement procedure should include calibration and zero-line operation before and after the operation under the same conditions (may be repeated multiple times).

(6) Preheat the calorimeter and sample to 10K to 15K of the highest temperature in question. To stabilize the system, optimize heat transfer conditions and remove adsorbed water or residual solvent.

(7) For experiments at low temperatures, prevent water from condensing from the atmosphere or prevent the volatile components of the sample from condensing in the cold environment of the measurement system.

### **3. Analysis of the Change Law of Specific Heat Capacity**

Taking the commonly used nitrate as an example, the specific heat capacity data collected by different experimenters are collectively drawn into a graph. The experimental methods and experimental conditions of each experimenter will be analyzed. The available data are screened out.

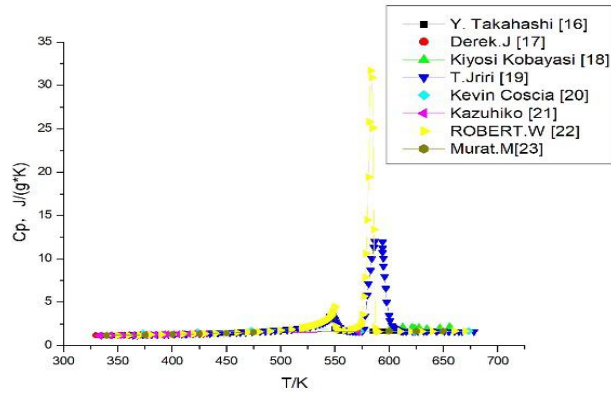


Figure 1: The relationship diagram of the specific heat capacity of NaNO<sub>3</sub> with temperature.

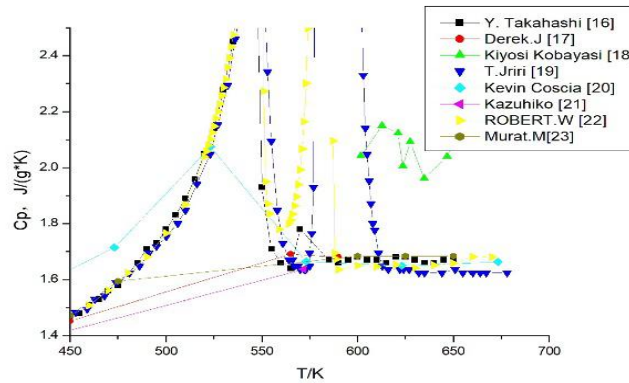


Figure 2: The relationship between the specific heat capacity of NaNO<sub>3</sub> in molten state and temperature.

It can be seen from Figure 1 and Figure 2 that it belongs to the solid state before the temperature reaches about 580K. The specific heat capacity of this state increases slowly with the increase of temperature. It is roughly in the solid-liquid coexistence zone at 580K-610K, where the molten salt gradually changes from solid to liquid. When the liquid transitions, the specific heat capacity increases sharply due to the existence of latent heat. At about 610K, the molten NaNO<sub>3</sub> salt completely becomes a liquid state. In this state, the specific heat remains almost unchanged with the increase in temperature.

In the molten state, except for the experimental data of Kiyosi Kobayasi [18], the specific heat capacity of NaNO<sub>3</sub> decreases slightly with increasing temperature. The authors of the other documents [16-17, 19-23] have shown through experiments that the specific heat capacity of NaNO<sub>3</sub> in the molten state remains almost unchanged with the increase of temperature.

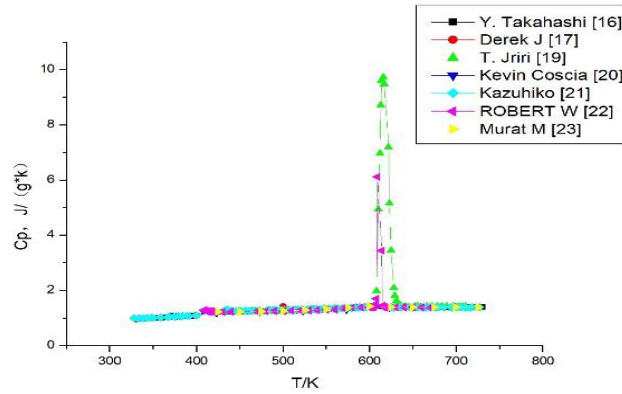


Figure 3: The relationship between the specific heat capacity of  $\text{KNO}_3$  and the temperature.

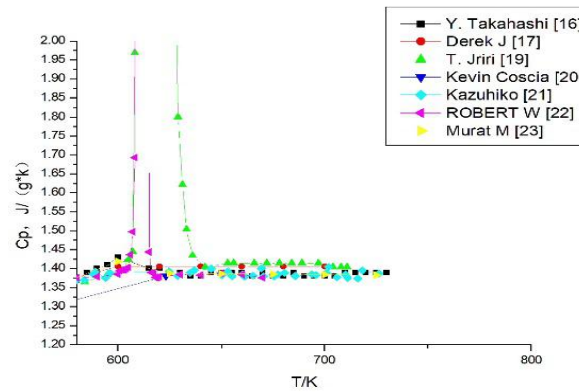


Figure 4: The relationship between the specific heat capacity of  $\text{KNO}_3$  in molten state and temperature.

From Figure 3 and Figure 4, it can be seen that the temperature is in the solid state before the temperature reaches about 600K. The specific heat capacity of this state increases slowly with the increase of temperature. 600K-630K belongs to the process of transition from solid to liquid. This state causes a sharp increase in specific heat capacity due to the existence of latent heat. Starting from 630K,  $\text{KNO}_3$  molten salt completely becomes a liquid state, in which the specific heat remains almost unchanged as the temperature rises.

In the molten state, the authors of the literature[16-17, 19-23] all show through experiments that the specific heat capacity of  $\text{KNO}_3$  in the molten state remains almost unchanged with the increase of temperature. It can be seen that the specific heat capacity values of  $\text{LiNO}_3$  measured by different experimenters are not much different at about  $1.38\text{J}/(\text{g}\cdot\text{K})$ , and the slight change in the value belongs to the acceptable range of random error.

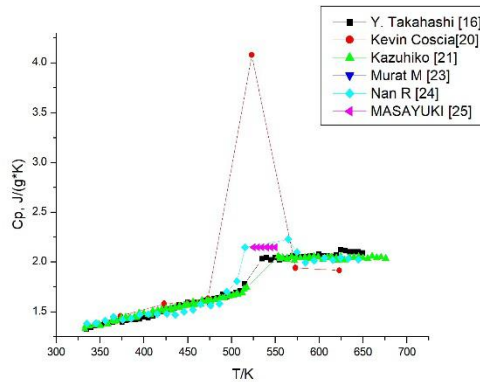


Figure 5: The relationship between the specific heat capacity of  $\text{LiNO}_3$  and the temperature.

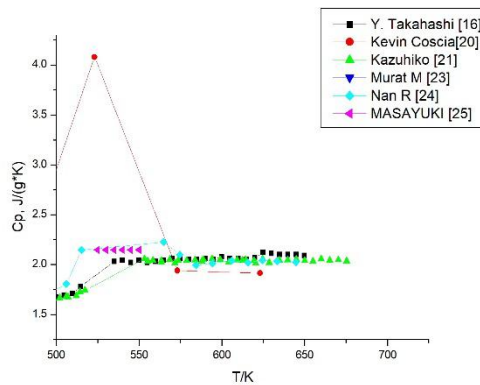


Figure 6: The relationship between the specific heat capacity of  $\text{LiNO}_3$  in molten state and temperature.

From Figure 5 and Figure 6, it can be seen that before the temperature reaches about 540K, it belongs to the solid state. The specific heat capacity of this state increases slowly with the increase of temperature. 540K-560K belongs to the process of transition from solid to liquid. This state causes a sharp increase in specific heat capacity due to the existence of latent heat. From 560K, the  $\text{LiNO}_3$  molten salt completely becomes a liquid state, in which the specific heat remains almost unchanged as the temperature rises.

In the molten state, the authors of literature[16,20-23,25] all show through experiments that the specific heat capacity of  $\text{LiNO}_3$  does not change with temperature in the molten state after stability. It can be seen that the specific heat capacity values of  $\text{LiNO}_3$  measured by different experimenters are not much different at about  $2.05\text{J}/(\text{g}\cdot\text{k})$ , and the slight numerical change belongs to the acceptable range of random error.

According to the above experimental data, it can be seen that in the molten state, the specific heat capacity values measured by different experimenters at the same temperature are inconsistent. There are many reasons for this phenomenon, one of which is that the temperature range of their solid-liquid coexistence zone is inconsistent (for example, the specific heat capacity of  $\text{LiNO}_3$  measured by the author MASAYUKI[25] has stabilized at 525K, which can be inferred from the author MASAYUKI The measurement of the melting point of  $\text{LiNO}_3$  and the temperature range of the solid-liquid coexistence zone are relatively advanced. In the solid-liquid coexistence zone, the solid changes to liquid. Due to the existence of latent heat, the specific heat capacity

changes in this zone are complicated. Schawe[26] indicated that different heating (or cooling) rates will affect the melting point of molten salt. The reason for this difference is due to the heat transfer path inside the sample and the smearing effect of the temperature curve, which leads to the sample temperature Relative to the measured temperature, there is a certain lag or lead. Similarly, GWHHöhne[11] indicated that due to the existence of noise when the machine is working, there will be an error of 2K-15K in the measurement of temperature T. The size of this error is determined by the sample itself and the type of phase transition of the sample.

#### 4. Conclusion

This article focuses on the study of the relationship between the specific heat capacity of the unary molten salt and the temperature, and Focus on the current differential scanning calorimetry method for measuring molten salt and some measures to minimize the error. After comparing the specific heat capacity data measured by different experimenters and summarizing and analyzing these data, the results show that in the molten state, part of the reason for the difference in this experimental values is because the temperature range of the solid-liquid coexistence zone is inconsistent. The experimental data that the specific heat capacity of monobasic nitrate in liquid state does not change significantly with the increase of temperature is more reliable. In the molten state, the specific heat capacity of  $\text{NaNO}_3$  is almost constant around  $1.65 \text{ j}/(\text{g}\cdot\text{k})$ , the specific heat capacity of  $\text{KNO}_3$  is almost constant around  $1.38 \text{ j}/(\text{g}\cdot\text{k})$ , and the specific heat capacity of  $\text{LiNO}_3$  is almost constant around  $2.05 \text{ j}/(\text{g}\cdot\text{k})$ . small changes belong to the acceptable range of random error. The filtered data of this paper can be used as the basis for predicting the specific heat capacity of the mixed molten salt.

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