# Measurement of Thermophysical Properties by Arbitrary Heating Method
## - Development of Pressure and Corrosion Resistance Measurement Unit -

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## SUMMARY

In order to measure thermophysical properties of $CaCl_2 \cdot nNH_3$ system as one of thermal storage systems, pressure and corrosion resistance measurement unit was developed, and effective thermal conductivity and thermal diffusivity were measured by arbitrary heating method. Effective thermal conductivity and effective thermal diffusivity of $CaCl_2$ only system in the temperature range of 290 K to 340 K were approximately constant, respectively. And then effective thermal conductivity and thermal diffusivity of $CaCl_2 \cdot 4NH_3$ system in the temperature range of 290 K to 350 K were approximately constant, respectively. No leak of the gas and no corrosion for this measurement cell were observed on the repeated measurements.

KEY WORDS: thermophysical properties, arbitrary heating method, calcium chloride, ammonia, pressure proof cell, thermal storage unit

## 1. INTRODUCTION

These days, some kinds of freons as the brine disrupt the ozone layer, and with increasing tendency of carbon dioxide and freons, the temperature on the earth is rising. Ammonia ($NH_3$) is presently attracting an attention as a promising working fluid, because $NH_3$ has no relation to disruption of the ozone layer and greenhouse effect on the earth.

For the sake of a thermal energy storage system utilizing low temperature heat sources such as solar energy or a hot effluent (approximately 353～373 K), the process using the chemical reaction of anhydrous salt with $NH_3$ has been proposed and discussed for its practicably. In this study, the chemical reaction of $CaCl_2 \cdot 4NH_3$ with $4NH_3$ was chosen here for the thermal energy storage system (see the following reversible chemical reaction: Ammoniation/Deammoniation), since this reaction can be driven by using low temperature heat sources.

Furthermore, the salt is low cost and easy to supply.

$$CaCl_2 \cdot 4NH_3 + 4NH_3 \iff CaCl_2 \cdot 8NH_3 + \Delta H$$

In the reversible reaction, $\Delta H$ (enthalpy change) is 43.8 kJ/mol-NH$_3$ at 0.1 MPa, 304 K [1], the value of which is considerably higher than the latent heat of vaporization of liquid NH$_3$, 23.4 kJ/mol-NH$_3$ at 0.1 MPa, 240 K [2]. Furthermore, this chemical reaction is well known as higher energy density system as compared with other reaction systems for energy storage system. In these studies, some prototypes of energy storage unit using CaCl$_2 \cdot$nNH$_3$ system were designed and discussed these performance [3,4,5,6].

However, thermophysical properties (e.g. effective thermal conductivity and thermal diffusivity) of CaCl$_2 \cdot$nNH$_3$ system for the sake of design as the thermal storage system have not measured. Furthermore, it is one of the difficult measurements to measure these thermophysical properties such as powder (solid - gas system) and with the chemical reaction.

Because it is necessary to establish various boundary conditions of measurement sample on general measurement methods of thermophysical properties. For example, the condition of constant temperature on steady state method, cyclic, pulse and step heating conditions and the constant heat flux of adiabatic, constant temperature and cooling condition on unsteady state method, which have fundamental necessity to establish various conditions. However, it is very difficult to satisfy these thermal conditions. Then, in this study, the measurement method, which is especially convenience to measure such as powder, grain and molten solid inserted in cylindrical or tubular vessel was adopted. In this measurement method, the temperature of powder sample and the boundary condition of heat flux are arbitrary. Therefore, in measuring time, heating and cooling conditions in this measurement method can be arbitrary.

In this study, thermophysical properties for CaCl$_2 \cdot$nNH$_3$ system were measured by arbitrary heating method using Laplace transform for cylindrical sample. This arbitrary heating method was developed by Iida *et al.*[7,8,9].

## 2. PRINCIPLE OF MEASUREMENT

In this study, this principle of measurement is only shown. Regarding the principle of this measurement method in detail, refer to arbitrary heating method by Iida *et al.*[7,8,9].

*2.1. Fundamental relation of heat conduction for one dimensional cylindrical coordinate*

Assuming heat flux is the direction of radius $r$ only, where $t$, $T$ and $\alpha$ are, respectively, time, temperature and thermal diffusivity, and $T(r,0) =$ constant, that is, initial temperature distribution is uniformity.

Considering $\theta(r,t)$ as temperature difference in equation (1),

$$\theta(r,t) = T(r,t) - T(r,0) \tag{1}$$

Fundamental heat conduction equation is given by

$$\frac{\partial \theta (r,t)}{\partial t} = \alpha \left\{ \frac{\partial^2 \theta (r,t)}{\partial r^2} + \frac{1}{r} \frac{\partial \theta (r,t)}{\partial r} \right\} \tag{2}$$

Equation (2) is transformed by using Laplace transformation and substitution of $\theta(r,0) = 0$ into equation (2), and then is rewritten to the ordinary differential equation, given by

$$\frac{d^2 \bar{\theta}}{dr^2} + \frac{1}{r} \frac{d\bar{\theta}}{dr} - \frac{s}{\alpha} \bar{\theta} = 0 \tag{3}$$

where $s$ is Laplace parameter.

However $\bar{\theta}$ is Laplace integration of $\{\theta(r,t)\}_{r=r} = \theta(t)$, which is defined by equation (4).

$$\bar{\theta} = \int_0^\infty e^{-st} \theta(t) dt \tag{4}$$

General solution of equation (3) is given by

$$\bar{\theta} = CI_0(\sqrt{s/\alpha} \cdot r) + DK_0(\sqrt{s/\alpha} \cdot r) \tag{5}$$

where $I_0$ and $K_0$ are modified Bessel functions of the first and the second kind of zero-order, respectively, and $C$ and $D$ are constants of integration, respectively.

On the other hand, heat flux $q(r,t)$ is given by Fourier's equation.

$$q(r,t) = -\lambda \frac{\partial T(r,t)}{\partial r} = -\lambda \frac{\partial \theta (r,t)}{\partial r} \tag{6}$$

where $\lambda$ is thermal conductivity.

Equation (6) is transformed by Laplace transform, and substitution of equation (5) into equation (6), then given by

$$\bar{q} = -\lambda \sqrt{\frac{s}{\alpha}} \left\{ CI_1(\sqrt{s/\alpha} \cdot r) + DK_1(\sqrt{s/\alpha} \cdot r) \right\} \tag{7}$$

*2.2. General principle of measurement*

Considering there is infinite tubular sample［Ⅰ］around infinite cylindrical sample［Ⅱ］, as shown in Figure 1, and assuming the heat flux is only direction of radius and the contact resistance is negligible, and the symbol $\times$ is expressed a measuring point of temperature. where measuring point 2 is defined as the boundary surface. And the temperature response $\theta(r_i,t)$ at each measuring point $i$ ($i$=1,2,3,4) is rewritten as $\theta_i(t)$, from equation (4), Laplace integration of each point is expressed by

$$\bar{\theta}_i = \int_0^\infty e^{-st} \theta_i(t) dt \tag{8}$$
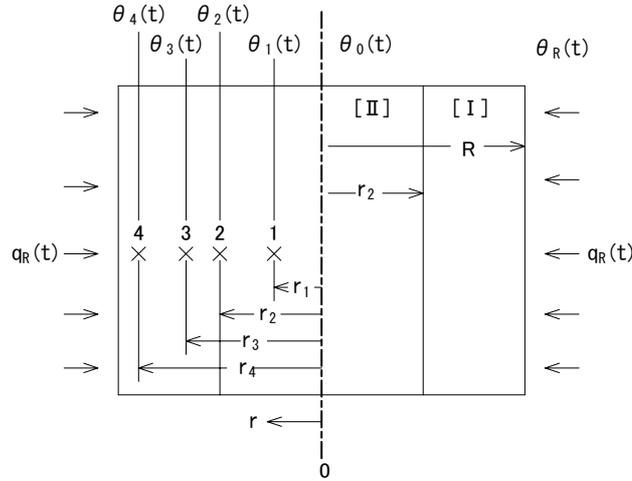
Figure 1. General principle of measurement.

### 2.2.1. Case of cylindrical sample

In this study, the supplied sample is the case of cylindrical sample [ II ]. Hence tubular sample[ I ] is the case of reference sample. Assuming $\alpha_{\mathrm{I}}$, $\lambda_{\mathrm{I}}$ and $c_{p\,\mathrm{I}} \times \rho_{\mathrm{I}}$ ($c_p$ : specific heat, $\rho$ :density)are, respectively, thermal diffusivity, thermal conductivity and heat capacity, and are well known. Hence measuring point 4 is not necessary. In [ II ], $q(0,t) = 0$ . Hence $(\bar{q})_{r=0} = 0$ . Thus $D_{\mathrm{II}} = 0$ in equation (7). Therefore, equation (5) is rewritten by

$$\bar{\theta} = C_{\mathrm{II}} I_0 (\sqrt{s / \alpha_{\mathrm{II}}} \cdot r_1) \tag{9}$$

Then, $\theta_1(t)$ and $\theta_2(t)$ are measured, and $\bar{\theta}_1$ and $\bar{\theta}_2$ are calculated from equation (8), and substitution of $\bar{\theta}_1$ and $\bar{\theta}_2$ into equation (9) and $C_{\mathrm{II}}$ is defined as equation (10), arranged by

$$C_{\mathrm{II}} = \bar{\theta}_1 / I_0 (\sqrt{s / \alpha_{\mathrm{II}}} \cdot r_1) \tag{10}$$

$$\bar{\theta}_1 I_0 (\sqrt{s / \alpha_{\mathrm{II}}} \cdot r_2) - \bar{\theta}_2 I_0 (\sqrt{s / \alpha_{\mathrm{II}}} \cdot r_1) = 0 \tag{11}$$

In equation (11), although unknown quantities are $\alpha_{\mathrm{II}}$ and $s$ , as far as the Laplace integration converges, equation (11) is set up for any positive finite value of $s$ . Therefore $\alpha_{\mathrm{II}}$ is determined from equation (11).

Next Laplace integration of heat flux in [ II ] at $r = r_2$ is given by substitution of $D_{\mathrm{II}} = 0$ into equation (7) and using equation (10). Equation (12) is given by

$$(\bar{q}_2)_{\mathrm{II}} = -\lambda_{\mathrm{II}} \sqrt{\frac{s}{\alpha_{\mathrm{II}}}} \bar{\theta}_1 \frac{I_1 (\sqrt{s / \alpha_{\mathrm{II}}} \cdot r_2)}{I_0 (\sqrt{s / \alpha_{\mathrm{II}}} \cdot r_1)} \tag{12}$$

On the other hand, In [ I ], $\bar{\theta}_2$ and $\bar{\theta}_3$ are calculated from measuring points $\theta_2(t)$ and $\theta_3(t)$ . Corresponding to $r = r_2$ and $r = r_3$ , respectively, and substitution of each $\bar{\theta}$ and $r$ into equation (5) and $C_{\mathrm{I}}$ and $D_{\mathrm{I}}$ are defined by as follows:

$$C_{\mathrm{I}} = \frac{\overline{\theta}_2 K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_3) - \overline{\theta}_3 K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2)}{I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_3) - I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_3) K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2)} \qquad (13)$$

$$D_{\mathrm{I}} = \frac{\overline{\theta}_2 I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_3) - \overline{\theta}_3 I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2)}{I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_3) K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) - I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_3)} \qquad (14)$$

Hence, Laplace integration of heat flux at $r = r_2$ in [ I ] is expressed from equation (7) with $C_{\mathrm{I}}$ and $D_{\mathrm{I}}$, as follows:

$$(\overline{q}_2)_{\mathrm{I}} = -\lambda_{\mathrm{I}}\sqrt{s/\alpha_{\mathrm{I}}}\left\{ C_{\mathrm{I}} I_1(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) - D_{\mathrm{I}} K_1(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) \right\} \qquad (15)$$

Clearly $(\overline{q}_2)_{\mathrm{II}} = (\overline{q}_2)_{\mathrm{I}}$, hence $\lambda_{\mathrm{II}}$ is determined from equation (16).

$$\frac{\lambda_{\mathrm{II}}}{\lambda_{\mathrm{I}}} = \sqrt{\frac{\alpha_{\mathrm{II}}}{\alpha_{\mathrm{I}}}} \frac{I_0(\sqrt{s/\alpha_{\mathrm{II}}} \cdot r_1)}{I_1(\sqrt{s/\alpha_{\mathrm{II}}} \cdot r_2)} \frac{1}{\overline{\theta}_1}\left\{ C_{\mathrm{I}} I_1(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) - D_{\mathrm{I}} K_1(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) \right\} \qquad (16)$$

*2.2.2. Measurement of temperature of central point in cylindrical sample and surface of reference sample at the same time*

In this experiment, the measurement system by the temperature response of cylindrical sample as supplied sample was adopted, shown in Figure 2. From Figure 2, the temperature responses at $r = 0$, $r = r_2$ and $r = r_R$ are measured, In equation (11), the subscript 1 is rewritten as the subscript 0, and substitution of $I_0(0) = 1$, then given by

$$\overline{\theta}_0 I_0(\sqrt{s/\alpha_{\mathrm{II}}} \cdot r_2) - \overline{\theta}_2 = 0 \qquad (17)$$

Hence, in this case, $\overline{\theta}_2/\overline{\theta}_0$ is calculated. Thermal diffusivity $\alpha_{\mathrm{II}}$ is calculated from Figure 3 immediately. where for thermal conductivity $\lambda_{\mathrm{II}}$, substitution of $r_1 \to 0$, $r_3 \to R$ and $\overline{\theta}_3 \to \overline{\theta}_R$ into equations (16), (13) and (14), respectively, give thermal conductivity $\lambda_{\mathrm{II}}$ as the following equation.

$$\frac{\lambda_{\mathrm{II}}}{\lambda_{\mathrm{I}}} = \sqrt{\frac{\alpha_{\mathrm{II}}}{\alpha_{\mathrm{I}}}} \frac{1}{I_1(\sqrt{s/\alpha_{\mathrm{II}}} \cdot r_2)} \frac{1}{\overline{\theta}_0}\left\{ C_{\mathrm{I}} I_1(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) - D_{\mathrm{I}} K_1(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) \right\} \qquad (18)$$

Then $C_{\mathrm{I}}$ and $D_{\mathrm{I}}$ are given by

$$C_{\mathrm{I}} = \frac{\overline{\theta}_2 K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot R) - \overline{\theta}_R K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2)}{I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot R) - I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot R) K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2)} \qquad (19)$$

$$D_{\mathrm{I}} = \frac{\overline{\theta}_2 I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot R) - \overline{\theta}_R I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2)}{I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot R) K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) - I_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot r_2) K_0(\sqrt{s/\alpha_{\mathrm{I}}} \cdot R)} \qquad (20)$$

Regarding the range of Laplace integration,

Since $e^{-st}\theta_i(t)dt$ is the function, which converges to zero with increasing $t$. Values of $s$ and $t_{max}$ can be determined from the following equation.

$$\int_0^\infty e^{-st}\theta_i(t)dt \doteqdot \int_0^{t_{max}} e^{-st}\theta_i(t)dt$$

where $st_{max}$ is expressed as following equation from Iida et *al*.[9].

$$8 \leqq st_{max} \leqq 12$$

In this experiment, $s$ was determined to satisfy $st_{max} = 10$.
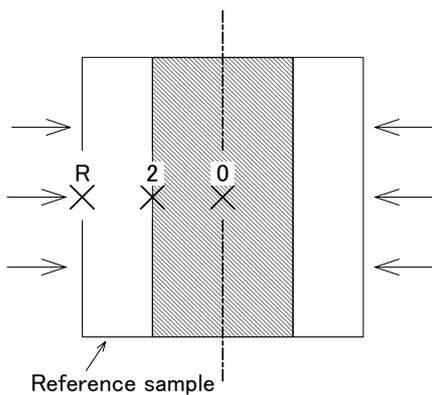
Figure 2. Measurement system.
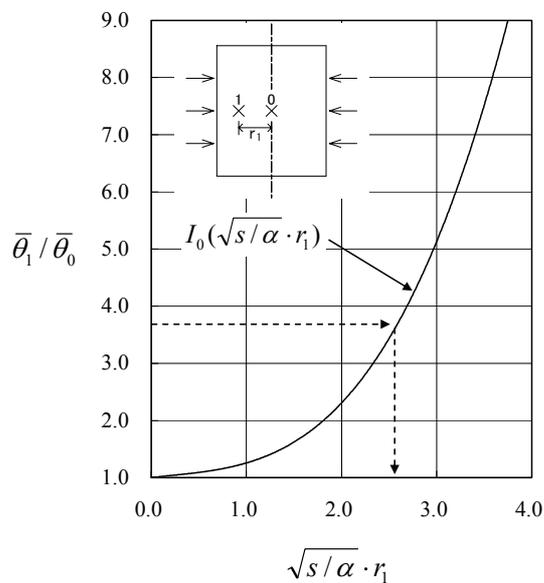
Figure 3. Determination of thermal diffusivity for temperature
measurement of central point.

## 3. EXPERIMENTAL SECTION

*3.1. Materials*

   CaCl$_2$ used in the experiment is produced by Wako Pure Chemical Industries Ltd. Japan. It is guaranteed reagent grade, and it is specified as the pure grade having minimum purity of 95.0 %. CaCl$_2$ is used without further purification. NH$_3$ gas of 99.99 % purity is provided from Seitetsu Kagaku Co. Ltd.

*3.2. Experimental apparatus*

Figure 4 schematically shows the experimental apparatus of the measurement system. This system consists of measurement unit (cell) as the reactor, $NH_3$ glass vessel, pressure regulator valve, pressure gauges, thermocouples and constant temperature water bath. The measurement cell is made of stainless steel and it is covered with water jacket, which can control the temperature in the measurement cell. The $NH_3$ vessel is pressure resistance glass vessel, which volume is $0.3 \times 10^{-3} \, m^3$, (up to 2.0 MPa), and the volume of the liquid $NH_3$ is measured by a microscope with an accuracy of $\pm 0.05$ % of full volume ($0.5 \times 10^{-3} \, m^3$).

In order to insulate the measurement unit from the surroundings, the apparatus is wrapped foamed polystyrol. The temperature in this unit is measured by using C-A type thermocouples by digital thermometer and the temperature data as the digital signal (change of mV) transferred to the micro computer and are analyzed.

The amount of liquid $NH_3$ transferred to the measurement cell from the $NH_3$ vessel can be measured by microscope. The temperature of the measurement cell, unit and the $NH_3$ vessel are controlled by using constant temperature bath having minimum accuracy within $\pm 0.1$ K separately.

The pressure in the vessels in measured by Bourdon gauge, which accuracy is $\pm 0.1$ % of full scale (up to 2.0 MPa). The pressure control in the measurement cell is carried out using the pressure regulator valve.



1: Measurement cell, 2: Pyrex glass vessel,
3: Pressure gauge, 4: Pressure regulator valve,
5: Constant temperature bath, 6: Pump,
7: Thermocouple, 8: Digital thermometer,
9: Micro Computer, 10: Temperature controller,
11: Water jacket
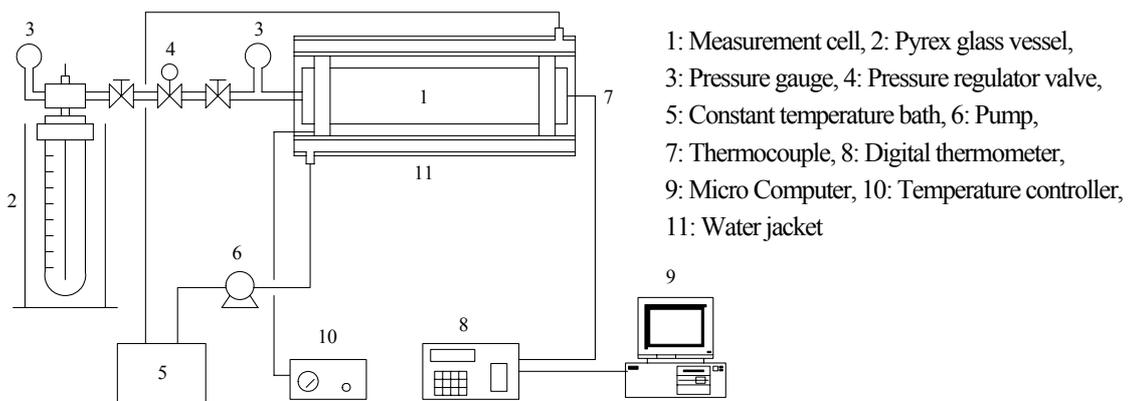
Figure 4. Schematic diagram of measurement unit.

Figure 5 shows the measurement cell in detail. This measurement cell consists of two major units, stainless steel pipe (Length: 230 mm, OD: 76.3 mm, ID: 68.3 mm) and reinforced pressure proof glass tube as the reference sample (Pyrex 7740: OD: 40.0 mm, ID: 32.0 mm) , and the temperature response is measured by the stainless steel covered C-A thermocouple ( $\phi$ 0.65 mm), which were inserted in the measurement cell.

The temperature of this measurement cell is increased and controlled by using the heater (Ni-Cr wire: $\phi$ 2 mm) and thermistor type temperature controller having minimum accuracy $\pm 0.1$ K.

In order to escape ununiform temperature field and to decrease heat resistance, $Al_2O_3$ powder is packed between stainless steel pipe and reference sample in this measurement cell.
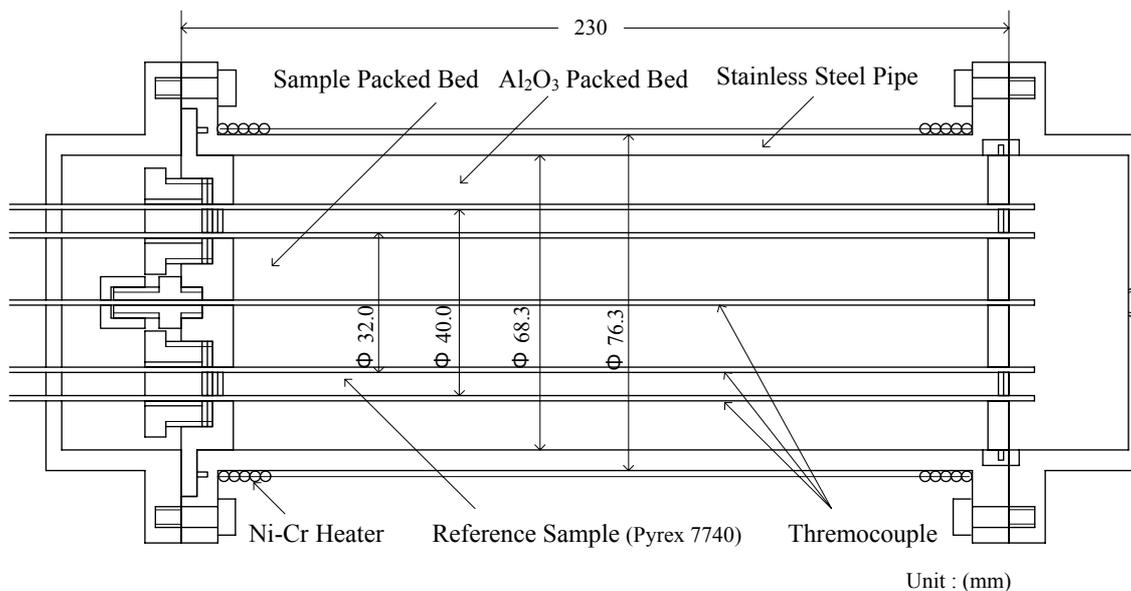
Figure 5. Measurement cell.

## 3.3. Experimental Procedure

In this experiment, thermopysical properties for $CaCl_2$ only system and $CaCl_2 \cdot 4NH3$ system were measured.

### 3.3.1. Preparing for CaCl₂ only system

$CaCl_2$ was crushed to a size below 200 JIS mesh. and was oven-dried at 773 K for approximately 5 hours. A dried $CaCl_2$ of 1.31 mole (approximately 145.2 g) was placed in the measurement cell, and this measurement cell was sealed. Then the preparing for measurement sample is finished.

### 3.3.2 Preparing for CaCl₂·4NH₃ system (Ammoniation)

$CaCl_2$ of 0.218 mole (approximately 24.2 g) was crushed below size of 200 JIS mesh and was dried at 773 K approximately for 5 hours by an oven.. A dried powder sample was placed in the measurement cell. It was sealed, and worked by the vacuum pump in order to remove air and any water from this measurement cell .

The $NH_3$ vessel was also evacuated for 2 hours and $NH_3$ gas introduced from the cylinder into the $NH_3$ vessel, which was kept at constant temperature (273 K) by cooling liquid. After liquid $NH_3$ was charged in it, its volume was measured by microscope rapidly and recorded. Then this measurement cell was connected with the $NH_3$ vessel shown in Figure 4. $NH_3$ gas moved to the measurement cell through the pressure regulator valve keeping constant pressure (0.5 MPa) during the reaction. The level of liquid $NH_3$ in the $NH_3$ vessel was measured by reading the scale of the $NH_3$ vessel using microscope, and mole number of $NH_3$ absorbed to pure $CaCl_2$ was calculated from this volume change.

When 4 moles of $NH_3$ was absorbed to the pure $CaCl_2$, the experiment of ammoniation is just finished.

*3.3.3 Measurement of thermal properties*

First, after temperature of cell is settled with measurement temperature and the temperature of measuring points are stabilized, and start heating of the measurement cell by charging electricity to Ni-Cr wire, where heating rate and maximum heating temperature are 5 K/min. and 10 K, respectively, in order to avoid violent reaction in the measurement cell during the measuring time. Temperature changes (change of mV) of C-A type thermocouple are measured by digital thermo meter and input was recorded to micro computer system, and the scan rate is every 9 seconds and the measurement time is 30 minutes.

# 4. RESULTS AND DISCUSSION

Figure 6 shows relation between temperature and thermal properties of $CaCl_2$ only system. In the measuring temperature range of 290 K to 340 K, effective thermal conductivity, $\lambda$ and effective thermal diffusivity, $\alpha$ were approximately constant (0.75 W/(m·K) and $0.15 \times 10^{-6}$ m$^2$/s, respectively) at atmospheric pressure. It is found that these thermal properties are almost independence of the measuring temperature range. And it has not been found a comparative data of these thermal properties.

Figure 7 shows relation between temperature and thermal properties of $CaCl_2 \cdot 4NH_3$. Effective thermal conductivity, $\lambda$ and effective thermal diffusivity, $\alpha$ were approximately constant (0.2 W/(m·K) and $0.75 \times 10^{-6}$ m$^2$/s, respectively) in the measuring temperature range of 290 K to 350 K. This system indicates similar tendency of $CaCl_2$ only system.
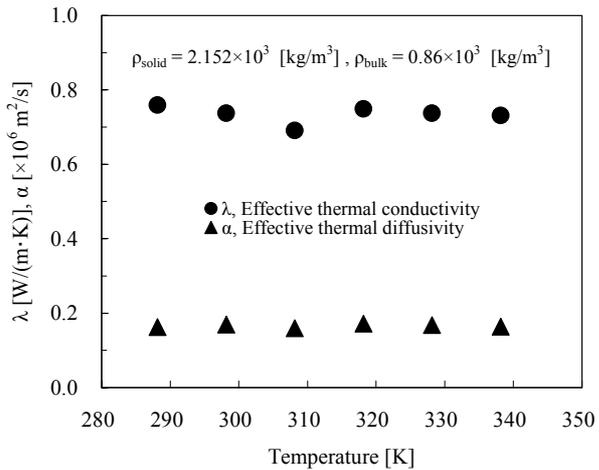


Figure 6. Relation between temperature and thermal
properties of $CaCl_2$ only system.
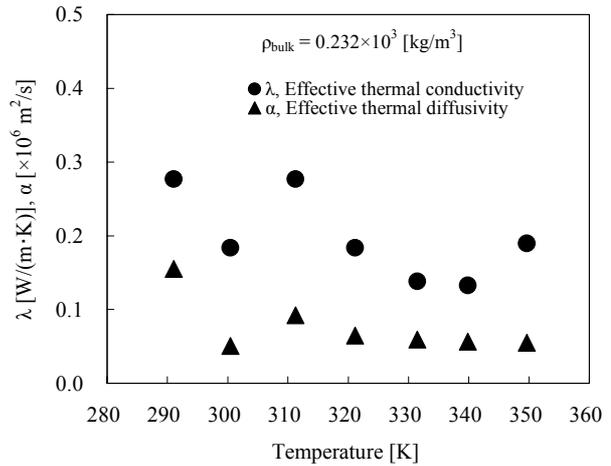
Figure 7. Relation between temperature and thermal
properties of $CaCl_2 \cdot 4NH_3$ system.

Figure 8 shows relation between temperature, pressure in the measurement cell and effective thermal conductivity.

From Figure 8, effective thermal conductivity did not increase in the range of at high temperature and high pressure in the measurement cell.
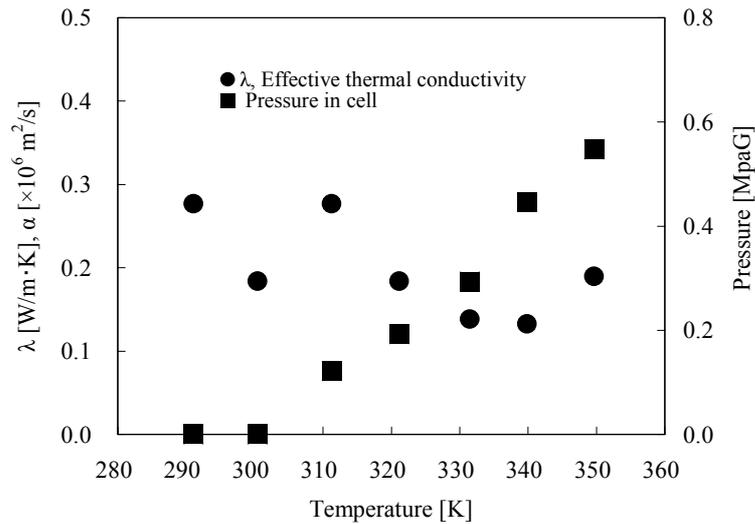


Figure 8. Relation between temperature and pressure in the measurement cell
and effective thermal conductivity.

Figures 7 and 8, in the measuring temperature range of 290 K to 310 K, it is found that the values of $\lambda$ and $\alpha$ vary widely. On the other hand, it is well known thermopysical properties of such as powders and porous solids depend on the void fraction (packed density), the fluid contained and the pressure of system in literatures. Particularly, in this experiment, it can be indicated that the void fraction (low packed density) and the pressure (low pressure: lower than atmospheric pressure) of system influence thermopysical properties.

No leak and no corrosion for this measurement unit were observed on the repeated measurements.
It is found that this measurement unit is applicable for thermal storage working media of high pressure and corrosion such as $NH_3$.

# 5. CONCLUSIONS

In this study, in order to measure thermopysical properties of $CaCl_2$ only system and $CaCl_2 \cdot 4NH_3$ system, the pressure and corrosion resistance measurement unit was developed, and the effective thermal conductivity and the effective thermal diffusivity of those systems were measured by arbitrary heating method. Both thermopysical properties were approximately constant in the measuring temperature and pressure range. It is found that these thermopysical properties are almost independence of the measuring temperature and pressure range.

No leak of the gas and no corrosion for this measurement cell were observed on the repeated measurements. It is

found that this measurement unit is applicable for thermal storage working media of high pressure and corrosion such as NH₃, and the data of these thermopysical properties of those systems are available for the design of thermal energy storage system.

## ACKNOWLEDGEMENTS

## NOMENCLATURE

$\alpha$     = thermal diffusivity and effective thermal diffusivity [m$^2$/s]

$\theta$     = temperature difference [K]

$\bar{\theta}$     = Laplace integration of $\theta$ [-]

$\lambda$     = thermal conductivity and effective thermal conductivity [W/(m·K)]

$\rho$     = bulk density [kg/m$^3$]

$c_p$     = specific heat [kJ/(kg·K)]

$C, D$     = constants of integration [-]

$I_0$     = modified Bessel function of the first kind of zero-order [-]

$K_0$     = modified Bessel function of the second kind of zero-order [-]

$q$     = heat flux [W/m$^2$]

$\bar{q}$     = Laplace integration of $q$ [-]

$r$     = radius [mm]

$R$     = outer diameter of sample [mm]

$s$     = Laplace parameter [-]

$t$     = time [s]

$t_{max}$     = time step of measuring time [s]

$T$     = temperature [K]

Scripts

I     = sample ［Ⅰ］

Ⅱ     = sample ［Ⅱ］

$i$     = measuring point

# REFERENCES

1) Yoneda, N. and Hagiwara, I. (1979). "Study of Chemical Heat Pump for Thermal Energy Storage". *Solar Energy*, 5, 4, pp.4-15.

2) Wentworth, W. E. and Jhonston, D. W. (1981). "Chemical Heat Pumps Using a Dispersion of a Metal Salt Ammoniate in an Inert Solvent". *Solar Energy*, 26, pp.141-146.

3) Hall, C. A. (1976). "DEVELOPMENT OF AMMONIATED SALTS THERMOCHEMICAL ENERGY STORAGE SYSTEMS Phase I ". U.S. Department of Energy.

4) Jeager, F, A., Haas, W. R. and Anderson, J. E. (1979). "DEVELOPMENT OF AMMONIATED SALTS THERMOCHEMICAL ENERGY STORAGE SYSTEMS Phase II ". U.S. Department of Energy.

5) Sakamoto,Y.and Yamamoto, H. (1990). "Performance of Thermal Storage Unit Using $CaCl_2$-$NH_3$ System Mixed with Ti". *The Canadian Journal of Chem.Eng* ., 68, pp.948-951.

6) Sakamoto,Y.and Yamamoto, H. (1995). "Effect of Metal Additive on The Performance of Horizontal Thermal Energy Storage Unit Using $CaCl_2$-$NH_3$ system". in Proceedings of *The 2nd International Conference on New Energy Systems and Conversions*, 31.July-4.August, Istanbul, Turkey pp.419-428.

7) Iida,Y. and Shigeta, H. (1981). "Measurement of Thermal Properties of Solids by Arbitrary Heating: 1st report". *The Japan Society of Mechanical Engineers (JSME) International Journal*, 47, pp.470-477. (in Japanese).

8) Iida,Y. and Shigeta, H. (1981). "Measurement of Thermopysical Properties of Solids by Arbitrary Heating: 2nd report". *The Japan Society of Mechanical Engineers (JSME) International Journal*, 47, pp.2324-2332. (in Japanese).

9) Iida,Y., Shigeta, H. and Akimoto, H. (1982). "Measurement of Thermopysical Properties of Solids by Arbitrary Heating: 2nd report". *The Japan Society of Mechanical Engineers (JSME) International Journal*, 48, pp.142-148. (in Japanese).