

vessels with other types of impeller, such as gate and paddle impellers.

Nomenclature

c	= clearance between blade and wall	[m]
D	= vessel diameter	[m]
d	= impeller diameter	[m]
L	= height of vessel	[m]
n	= rotational speed of impeller	[s ⁻¹]
P	= non-dimensional pressure	[—]
p	= static pressure	[Pa]
Q	= inlet flow rate	[m ³ /s]
R, Z	= non-dimensional coordinates	[—]
Re	= Reynolds number ($= d^2 n \rho / \mu$)	[—]
r, z	= r - and z -coordinates, respectively	[m]
r_1, r_2, r_3, z_1, z_2	= geometrical variables shown in Fig. 1	[m]
V_R, V_z, V_θ	= non-dimensional velocities	[—]
v_r, v_z, v_θ	= velocities in r -, z - and θ -directions, respectively	[m/s]
w	= blade width	[m]
ζ	= non-dimensional vorticity	[—]
θ	= θ -coordinate	[—]
μ	= viscosity	[Pa · s]

ρ	= density	[kg/m ³]
ψ	= non-dimensional stream function	[—]
ω	= angular velocity	[s ⁻¹]

<Subscript>

W = wall

<Superscript>

n = n -th iterative value

Literature Cited

- 1) Hiraoka, S., I. Yamada and K. Mizoguchi: *J. Chem. Eng. Japan*, **11**, 487 (1978).
- 2) Kuriyama, M., H. Inomata, K. Arai and S. Saito: *AIChE J.*, **28**, 385 (1982).
- 3) Kuriyama, M., K. Arai and S. Saito: Preprints for the 17th Autumn Meeting of the Soc. of Chem. Eng., Japan, SM112, Sendai (1983).
- 4) Murakami, Y., K. Fujimoto, T. Shimada, A. Yamada and K. Asano: *J. Chem. Eng. Japan*, **5**, 297 (1972).
- 5) Peters, D. C. and J. M. Smith: *Trans. Instn. Chem. Engrs.*, **45**, T360 (1967).
- 6) Smith, J. M.: *Chem. Engrs.*, CE45 (1970).
- 7) Takahashi, K., M. Sasaki, K. Arai and S. Saito: *J. Chem. Eng. Japan*, **15**, 217 (1982).

A CONSIDERATION OF THE EFFECT OF PHONON ON THERMAL CONDUCTIVITY DURING THE COURSE OF REACTION STATE

HITOKI MATSUDA AND MASANOBU HASATANI

Department of Chemical Engineering, Nagoya University, Nagoya 464

Key Words: Thermal Conductivity, Silver Iodide, Crystal Transformation, Differential Thermal Analysis, Heat Conduction Mechanism, Electrical Conductivity

Introduction

Thermal conductivity is one of the most important thermophysical properties in the evaluation of the heat flow rate within a solid. Up to the present time, various methods like the absolute method, the twin plate method, the hot wire method,^{12,16)} and the Laplace transform method³⁾ have been proposed for the thermal conductivity measurement of solids. These conventional methods, however, cannot be used for measurements of thermal conductivity when the materials to be measured are in the course of phase change or chemical reaction. It is difficult in these methods to eliminate the additional heat flow

released by phase change or reaction from the total heat flow.

The present authors⁷⁻⁹⁾ previously showed that by applying the principle of D.T.A. (differential thermal analysis) the thermal conductivity of a solid during phase change or reaction could be determined from the peak area of the D.T.A. curve and that the heat of phase change or reaction could be virtually eliminated from the measurement system.

From the results of measurements carried out on several kinds of solid materials, the thermal conductivities during reaction were found to take an almost constant value, smaller than those in both the pre- and the post-reaction states.⁷⁾ In the case of melting and/or solidification of organic polymers, the value is approximately equal to that in the liquid state.⁹⁾

Received June 19, 1984. Correspondence concerning this article should be addressed to M. Hasatani.

Furthermore, the thermal conductivity in the course of reaction was found to be vigorously affected by the heat of reaction, that is, the ratio of the thermal conductivity during reaction to that in the pre-reaction state decreases with increase of reaction heat, and finally reaches an asymptotic value.⁸⁾

To elucidate the above-mentioned behaviour of the thermal conductivity change in the course of phase change or reaction, further works on the following two subjects are considered necessary: the effect of thermal conductivity in the course of reaction on the overall heat conduction rate, and the mechanism of heat conduction through a solid in the course of reaction. The former subject was already partly discussed elsewhere.¹⁰⁾ The latter subject involves more substantial features but may be difficult to solve. The present work is concerned with an approach to solving the latter problem.

As is well known, silver iodide undergoes a crystal transformation ($\alpha \rightleftharpoons \beta, \gamma$ form) at about 420.2 K, and the electrical conductivity of the α -phase of silver iodide is known to increase by more than three orders of magnitude compared with those of the β - or γ -phase.¹⁵⁾ Silver iodide is a typical semiconductor and this trend in electrical conductivity is considered to be closely related to the change in behaviour of crystal-line and ion through the phase transition.

With respect to the thermal conductivity of silver iodide in the non-reaction state, λ , a few data were reported by Mogilevsky and Chundnovsky,¹¹⁾ Bremer and Nölting,¹⁾ and Touloukian *et al.*¹⁴⁾ These thermal conductivity data are, however, not so sufficient for practical use. Thus, in the present study, the thermal conductivity of silver iodide was measured in the temperature range from 298.2 to 503.2 K, which involves the transition temperature.

As a result of the present work, it was found that the obtained value of the thermal conductivity of silver iodide in the course of crystal transformation, Λ , was $(0.142 \pm 0.007) \text{ W/m} \cdot \text{K}$, which was about 22% smaller than the thermal conductivities in both the pre- and the post-reaction states, λ . Further, it was found that this value of $\Lambda/\lambda \approx 0.78$ could be well correlated with those of the other reactions in accordance with the relation between Λ/λ and the heat of reaction.⁸⁾

1. Experimental

Commercial silver iodide powder, the purity of which was about 99% (manufactured by Kishida Chemical Co., Ltd.) was pressed by an oil press to form a cylindrical shape, $7.5 \times 10^{-4} \text{ m}$ in diameter, $2.0 \times 10^{-3} \text{ m}$ in height (the density, $\rho = 5030 \text{ kg/m}^3$). The thermal conductivity during the course of the crystal transformation was measured by applying the principle of D.T.A. The experimental apparatus and

the procedures were almost the same as those reported in the authors' previous papers.⁷⁻⁹⁾ The thermal conductivity of silver iodide in both the pre- and post-phase transitions was measured by the hot wire method¹²⁾ over the temperature range between 298.2 and 503.2 K.

2. Results

2.1 Thermal conductivity of silver iodide

The obtained results of Λ are plotted against the absolute temperature together with those of λ in Fig. 1. It is seen from Fig. 1 that the value of λ decreases from about $0.29 \text{ W/m} \cdot \text{K}$ at room temperature to about $0.18 \text{ W/m} \cdot \text{K}$ at 410.2 K with rising temperature, and that at about 420.2 K (phase transition point) λ drops to a value of $\Lambda \approx 0.142 \text{ W/m} \cdot \text{K}$. After completion of the phase transition λ returns to an almost constant value of about $0.182 \text{ W/m} \cdot \text{K}$ over the temperature range up to 503.2 K. The value of Λ was found to be about 22% smaller than both the thermal conductivities at 410.2 K (pre-reaction state) and at 430.2–503.2 K (post-reaction state).

2.2 Electrical conductivity of silver iodide

Typical examples of the electrical conductivity of silver iodide in heating and cooling processes are shown in Fig. 2, which shows the reform of the data measured by Ikeda⁴⁾ by use of a 1 kHz impedance bridge. It is seen from Fig. 2 that the electrical conductivity of silver iodide increases in proportion to temperature during the heating process, and that the conductivity curve shows an abrupt change at about 420.2 K, this temperature corresponding to the transition point of silver iodide from the β and γ to the α phase. The electrical conductivity of silver iodide is in the order of magnitude of $10^{-4} (\Omega \cdot \text{m})^{-1}$ at room temperature, while above 420.2 K (in the α phase) it shows an extremely high value in the order of magnitude of $10^2 (\Omega \cdot \text{m})^{-1}$. The charge carrier in the α phase was found to be only the silver ion by Tubandt and Lorentz,¹⁵⁾ and the value above 420.2 K is considered the ionic conductivity. In Fig. 2, a similar result of electrical conductivity behaviour is observed in the cooling process during the phase transition from the α to the β form. There exists, however, a slight difference between the curves for heating and cooling processes in temperature. This may be due to supercooling of the α -phase.

This anomaly in behaviour of the electrical conductivity of silver iodide is ascribed to the increase of imperfections in the crystal lattice (in this case, Frenkel defects). That is, in α -silver iodide the silver ion can move relatively easily from void to void in the iodine-ion framework, and therefore the ionic conductivity shows a higher value in this crystal structure.

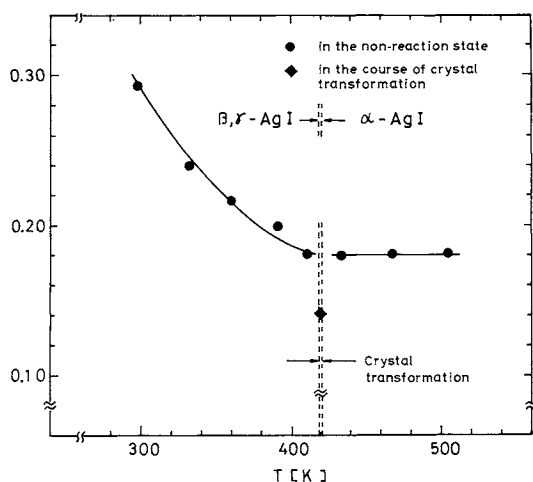


Fig. 1. Effective thermal conductivity of silver iodide ($\rho = 5030 \text{ kg/m}^3$).

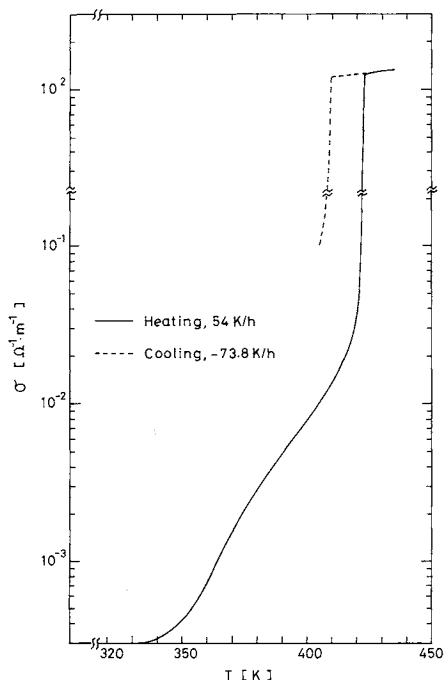


Fig. 2. Typical examples of electrical conductivities of silver iodide in heating and cooling processes.

3. Discussion

The thermal conductivity data of silver iodide shown in Fig. 1 are all the effective thermal conductivities including the effect of the pores in the specimen. Then, two equations, the Kunii-Smith⁵⁾ and the Loeb⁶⁾ equations, were used to estimate the crystal thermal conductivity before the phase transition point, λ_s , from the measured data. **Figure 3** shows the relations of $\log \lambda_s$ vs. $\log T$. The solid line corresponds to the results from the Kunii-Smith equation, and the broken line, those from the Loeb equation. It is seen from the figure that both relations could be represented well by a straight line as

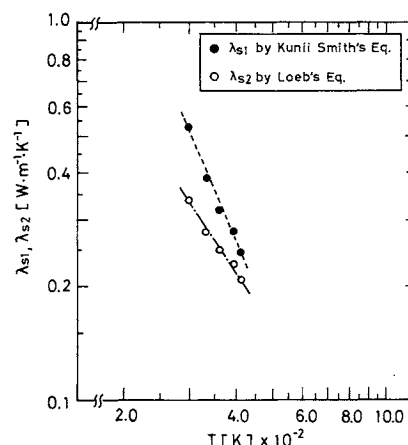


Fig. 3. Plots of $\log \lambda_s$ vs. $\log T$.

$$\lambda_s = C/T^n \quad (1)$$

From the slopes of these straight lines, the values of the index, n , were found to be 2.4 and 1.5 for the solid line and the broken line, respectively. Therefore, it is considered from this result that the principal mechanism of heat conduction through silver iodide in the temperature range from 298.2 to 410.2 K is due to the migration of phonon, although λ_s is not directly proportional to $1/T$ in this case. The values of n larger than unity may suggest that the mean free path of phonon in silver iodide might be reduced additionally by other scattering factors such as isotopes or impurities and dislocations.¹⁷⁾

In order to elucidate the reason why the thermal conductivity of α -silver iodide after the completion of crystal transformation is almost constant up to 503.2 K, it is necessary to make further examination as to whether the silver ions can be the heat carrier or not, since the contribution of the electrical thermal conduction based on the ionic conduction of silver ions to the overall thermal conductivity is not yet confirmed.

On the other hand, as to the mechanism of heat conduction during the course of reaction, the following tentative interpretation is proposed. In the course of crystal transformation, the crystal structure of silver iodide is considered to undergo once the disordered state which may be attributed to the formation or deformation of lattice defects, the temporary enhancement of the lattice vibration of the framework of iodine ions, etc. The anomalous change in the electrical conductivity may be caused by such a transitional change in the silver iodide crystal structure. The extraordinary increase of the specific heat of silver iodide in the course of crystal transformation¹³⁾ is also known to result from such transient behaviour of the silver iodide crystal.

In view of the above-mentioned background of the structural change of the silver iodide crystal during

crystal transformation, it is assumed that in this thermophysically unstable state the phonon conduction is disturbed by the tentative scattering of the lattice vibration in the course of rearrangement of the crystal structure. Therefore, it may be concluded that the decrease in thermal conductivity of silver iodide in the course of crystal transformation is due to a significant drop of the phonon conduction.

With reference to our consideration, Hedvall *et al.*²⁾ reported that the reactivity of silver iodide with barium oxide attains the maximum in the vicinity of the phase transition point of silver iodide. This phenomenon also may be evidence that in the course of crystal transformation the disordered state of silver iodide exists, which involves the active site in the molecular structure.

Acknowledgment

The authors wish to express their deep gratitude to Professor Osamu Yamamoto in Mie University for his instructive advice with respect to the electrical conductivity of silver iodide, and they also express their thanks to Dr. Y. Takai in Nagoya University for his useful suggestions on electrical conductivity measurements.

Nomenclature

C	= a constant	$[W \cdot K^{n-1} \cdot m^{-1}]$
n	= index	$[-]$
T	= absolute temperature	$[K]$
λ	= effective thermal conductivity in the course of reaction state	$[W \cdot m^{-1} \cdot K^{-1}]$
λ	= effective thermal conductivity in the non-reaction state	$[W \cdot m^{-1} \cdot K^{-1}]$

λ_s	= thermal conductivity of crystal solid material	$[W \cdot m^{-1} \cdot K^{-1}]$
ρ	= density of sample material	$[kg \cdot m^{-3}]$
σ	= electrical conductivity	$[\Omega^{-1} \cdot m^{-1}]$

Literature Cited

- 1) Bremer, F. and J. Nölting: *Ber. Bunsen-Gesellschaft*, **80**, No. 1, 12 (1976).
- 2) Hedvall, J. M., E. Gapring, N. Lindekrantz and L. Nelson: *Zeit. Anorg. und Allg. Chemie*, **197**, 399 (1931).
- 3) Iida, Y. and H. Shigeta: *Trans. JSME, B*, **47-415**, 470 (1981).
- 4) Ikeda, S.: *Ph. D. Thesis*, Nagoya University (1973).
- 5) Kunii, D. and J. M. Smith: *AIChE J.*, **6**, 97 (1960).
- 6) Loeb, A. L.: *J. Am. Ceram. Soc.*, **37**, 96 (1954).
- 7) Matsuda, H., M. Hasatani and S. Sugiyama: *Kagaku Kogaku Ronbunshu*, **1**, 589 (1975).
- 8) Matsuda, H., M. Hasatani and S. Sugiyama: *Kagaku Kogaku Ronbunshu*, **2**, 630 (1976).
- 9) Matsuda, H., M. Hasatani and S. Sugiyama: *Kagaku Kogaku Ronbunshu*, **7**, 355 (1981).
- 10) Matsuda, H., M. Hasatani and S. Sugiyama: *Kagaku Kogaku Ronbunshu*, **5**, 124 (1979).
- 11) Mogilevsky, B. M. and A. Ph. Chudnovsky: *Proc. Int. Conf. Phys. Semicond.* 9th, Bd. 2, 1241 (1968).
- 12) Nagasaka, K., M. Shimizu and S. Sugiyama: *J. Chem. Eng. Japan*, **6**, 264 (1973).
- 13) Nölting, J. and D. Rein: *Z. Physik. Chem.*, **NF66**, 150 (1969).
- 14) Touloukian, Y. S., R. W. Powell, C. Y. Ho and P. G. Klemens: "Thermophysical Properties of Matters," Vol. 2, p. 563, IFI/Plenum, New York, Washington (1970).
- 15) Tubandt, C. and E. Lorentz: *Z. Physik. Chem.*, **87**, 513 (1914).
- 16) Van der Held, E. F. M. and F. G. Van Drunen: *Physica*, **15**, 865 (1949).
- 17) Yamashita, J. and M. Fukuchi: "Kotai no Butsuri," pp. 131-146, Maruzen (1977).

UNSTEADY HEAT TRANSFER CHARACTERISTICS IN A SEMITRANSSPARENT MEDIUM HEATED BY DIFFUSE AND COLLIMATED RADIATION

YOSHINORI ITAYA, NORIO ARAI AND MASANOBU HASATANI

Department of Chemical Engineering, Nagoya University, Nagoya 464

Key Words: Heat Transfer, Solar Energy, Radiation, Solar Collector, Semitransparent Liquid, Diffuse Radiation, Collimated Radiation

Solar radiation energy incident to the surface of the earth consists of two components: collimated radiation characterized as direct-beam, and diffuse radiation resulting from multi-scattering of dust, aero-

sol, mist and other fine particles in the atmosphere.

In recent years, considerable research has been directed to the prediction of the fractional ratios of diffuse and collimated fluxes to the total incident solar radiation flux.^{6,7,9,11,12)} According to measurements in North America,^{9,12)} the contribution of diffuse

Received June 29, 1984. Correspondence concerning this article should be addressed to M. Hasatani.