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MEASUREMENT OF THERMOPHYSICAL PROPERTIES OF AMMONIUM SALTS IN THE SOLID AND MOLTEN STATES

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Abstract

The thermal conductivity, specific heat capacity and thermal diffusivity of solid and molten ammonium thiocyanate, ammonium formate, ammonium acetate and ammonium nitrate were measured in the temperature range 80–190°C, including the solid and liquid phases, by using the AC-heated strip (wire) technique. The results indicate that the thermal conductivities depend on the type of the ammonium salt. It was found that the mechanism of heat transfer is due to phonons in the region below the melting points of the salts, while above this region the main mechanism is due to conduction.

Keywords: ammonium salts

Introduction

In recent years, molten salts have been attracting attention as heat-transfer media or thermal storage materials at high temperature. Further, the molten salt breeder reactor is of special interest [1–3]. In the present work, the thermal conductivity (λ), thermal diffusivity (a) and specific heat capacity (ρc) have been measured for solid and liquid phases of ammonium thiocyanate (NH_4SCN), ammonium formate ($HCOONH_4$), ammonium acetate (CH_3COONH_4) and ammonium nitrate (NH_4NO_3), using the AC-heated wire method [4] in the temperature range 80–190°C.

Ammonia is a common, extremely useful compound that is produced commercially in huge quantities by the direct union of nitrogen and hydrogen. It is formed in nature by the decay of proteins in the bodies of dead plants and animals. It is used as a fertilizer, a refrigeration gas and a solvent. Ammonium nitrate is commonly used as an explosive in bombs and shells. Ammonium

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compounds as a class are noted for their great solubility in water. Most ammonium compounds are sufficiently stable to exist indefinitely at room temperature, but they decompose when heated.

Experimental

An ammonium salt of high purity grade was placed around the temperature oscillation sensor in a stainless steel cell, pre-melted and then cooled down to room temperature to attain a solid layer around the temperature oscillation heater and in good contact with it.

The theory of the plane temperature wave method was used to determine the thermal activity $b=\lambda/a^{1/2}$ of the investigated salt. In this case, the temperature oscillation heater in the experimental cell was in the form of a plane foil. The radial heat flow method was used to determine the thermal diffusivity. A thin wire (instead of a foil) was then used in the experimental cell. By means of these two methods, all the thermal properties of the sample (λ, a and ρc) were determined [5].

For determination of the thermal activity (b), a metallic foil was immersed in the melted salt under investigation to produce a plane temperature wave. The foil was heated by means of an alternating current with angular frequency w.

The amplitude of temperature oscillation (θ_o) of a strip is related to the thermal activity of the investigated sample according to the following formula:

$$b = \frac{d}{2}\left[\frac{1}{2}\left(\frac{W_o}{d\sqrt{w}S\theta_o}\right)^2 - 1\right]^{1/2} - 1 \tag{1}$$

where $d=\sqrt{w}(\rho C_p)_s h$, w_o is the power, S is the cross-sectional area of one side of the strip, $(\rho C_p)_s$ is the heat capacity of the strip material, and h is the thickness of the strip.

For determination of the thermal diffusivity (a), the amplitude of the temperature oscillations (θ) of the wire is related to the thermal properties of the sample and the wire heat capacity $(\rho C_p)_w$ according to the following relation:

$$\theta = \theta_o\left(\frac{\mathrm{her}^2(X) + \mathrm{hei}^2(X)}{[X\,\eta\,\mathrm{hei}(X) + \mathrm{her}'(X)]^2 + [X\,\eta\,\mathrm{her}(X) - \mathrm{hei}'(X)]^2}\right)^{1/2} \tag{2}$$

where $X=\sqrt{(2w/a)}r$, η is the ratio between the heat capacity of the specimen and the heat capacity of the wire, i.e. $\eta=(\rho C_p)_s/(2\rho C_p)_w$, r is the radius of the wire, ρ is the density, θ_o is the amplitude of the temperature oscillations of a noninertial strip, and her, hei, her′ and hei′ are Hankel functions and their derivatives. From Eqs (1) and (2), a, λ, and ρC_p for the sample under investigation can be calculated.

Results and discussion

The thermophysical properties of four solid and molten salts of ammonia were measured, and the data are illustrated in Figs 1–4. As shown in Fig. 1a, the thermal conductivity of ammonium thiocyanate (*m.p.* = 149.6°C) varies slightly with temperature in the ranges of the solid and liquid phases. However,

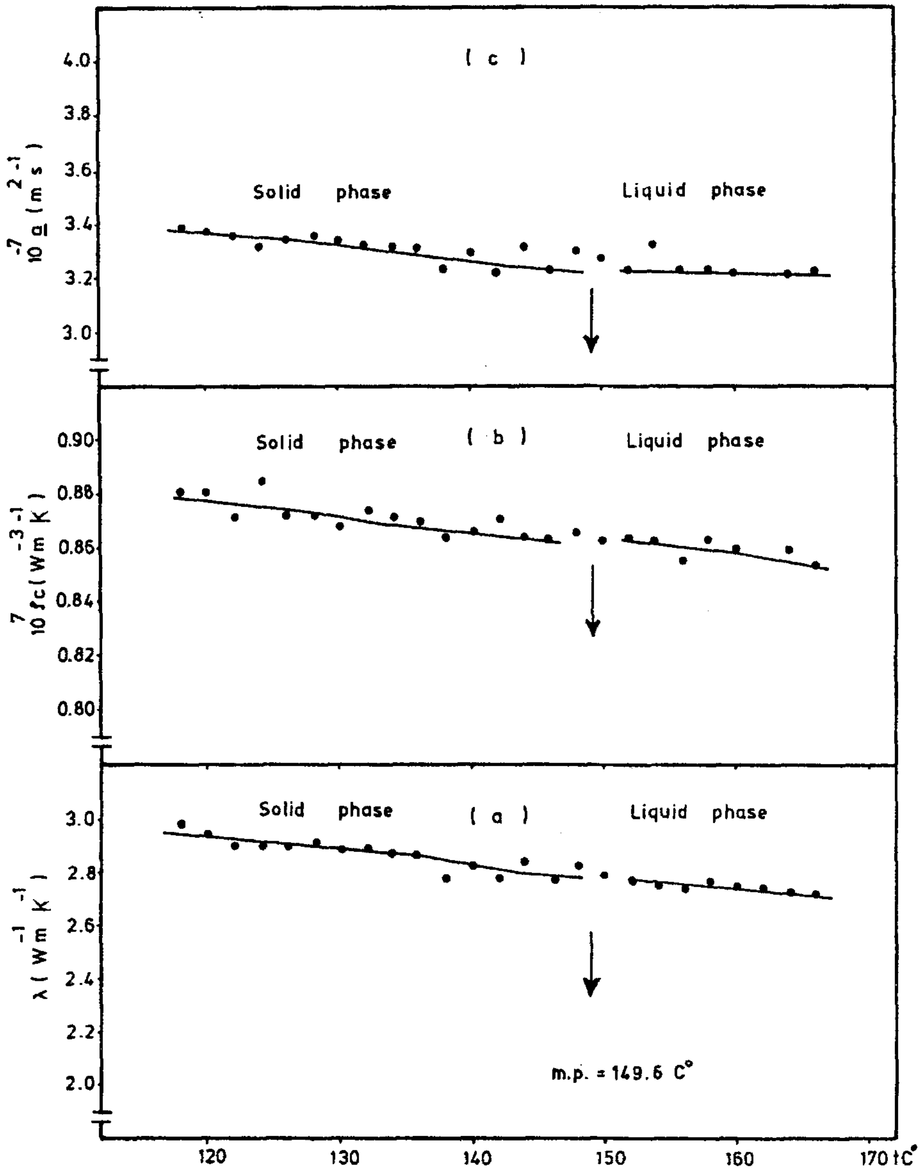

Fig. 1 Variation in (a) thermal conductivity, (b) specific heat capacity and (c) thermal diffusivity of ammonium thiocyanate (*m.p.* = 149.6°C) with temperature

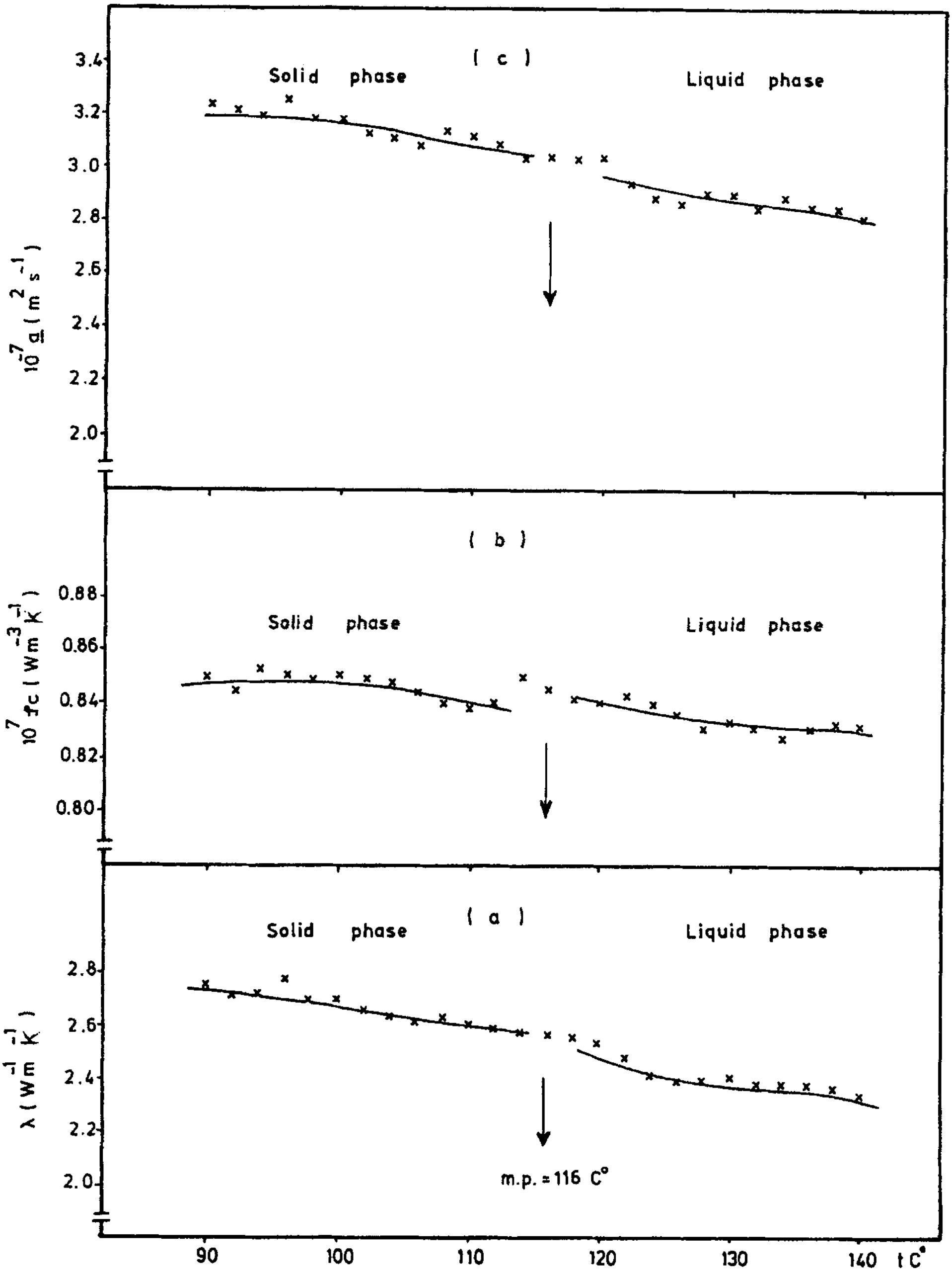

Fig. 2 Variation in (a) thermal conductivity, (b) specific heat capacity and (c) thermal diffusivity of ammonium formate (*m.p.* = 116°C) with temperature

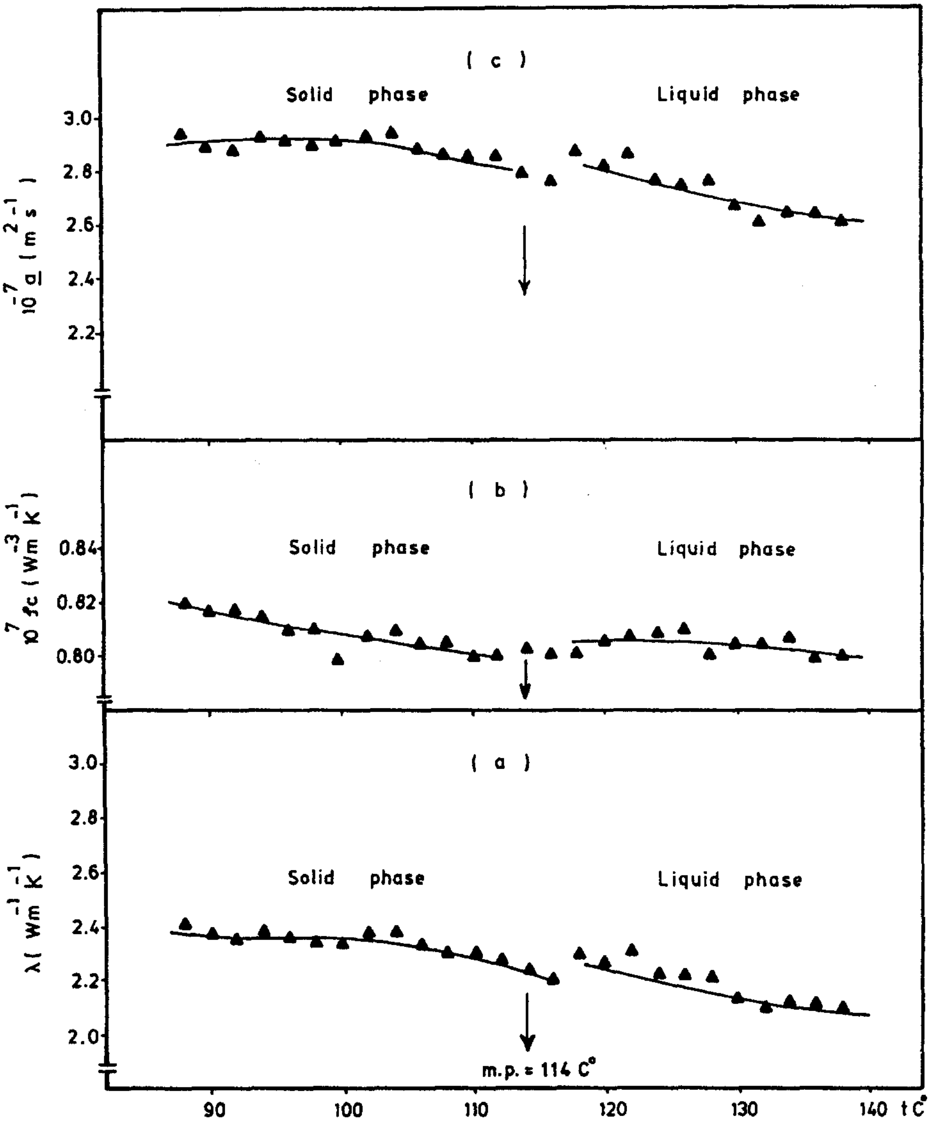

Fig. 3 Variation in (a) thermal conductivity, (b) specific heat capacity and (c) thermal diffusivity of ammonium acetate (*m.p.* = 114°C) with temperature

the thermal conductivity coefficient of ammonium thiocyanate is larger than those of the other investigated salts (see Figs 2a, 3a and 4a). The thermal conductivities increase in the sequence:

ammonium thiocyanate>ammonium formate>
ammonium acetate>ammonium nitrate

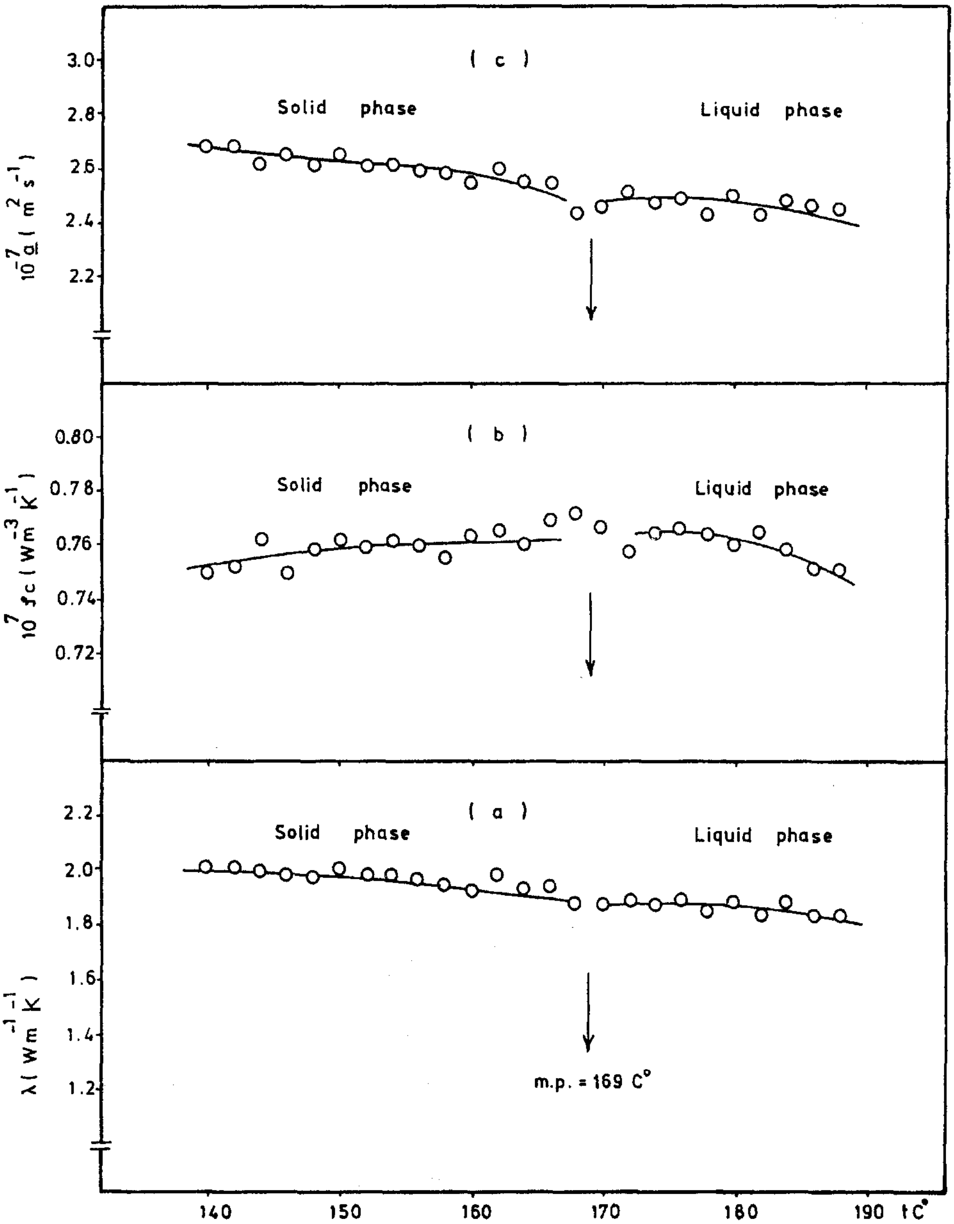

Fig. 4 Variation in (a) thermal conductivity, (b) specific heat capacity and (c) thermal diffusivity of ammonium nitrate (*m.p.* =169°C) with temperature

The conduction mechanism in liquids is more complicated because convective and radiative heat transport accompany the conduction process. For this reason, we use a liquid layer around the temperature oscillation sensor (foil or wire) that is thin enough to suppress hydrodynamic currents. This leads to elimination of the convective heat transport.

Figures 1b–4b show the changes in the specific heat capacities (ρc) of the ammonium salts with temperature. It was found that ρc is constant and obeys the Debye theory of specific heat at high temperature.

The thermal diffusivities a of the ammonium salts in both the solid and liquid states are presented in Figs 1c–4c. It was observed that a slightly decreases as the temperature increases in the solid and molten states. The thermal diffusivity is related to the total thermal conductivity by the relation:

$$a=\lambda/\rho c$$

where ρ is the density of the investigated material. From the values and behaviour of the thermal conductivity with change in temperature (λ decreases as temperature increases), we can conclude that the heat transfer through the investigated salts take place *via* phonons.

References

1 Y. Kato, K. Furukawa, N. Araki and K. Kobayasi, High Temp.-High Press., 15 (1983) 191.
2 N. Araki, M. Matsuura, A. Makino, T. Hirata and Y. Kato, Int. J. Thermophys., 9 (1988) 1071.
3 N. Araki and K. Kobayasi, Heat Trans., 14 (1985) 56.
4 S. R. Atalla, A. A. El-Sharkawy and F. A. Gasser, Int. J. Thermophys., 2 (1981) 155.
5 A. Z. Dakroury, M. B. S. Osman and A. A. El-Sharkawy, Int. J. Thermophys., 11 (1990) 515.