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Thermoelectric Powers of Molten I_2+Te Solutions

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The initial and steady-state potentials of thermocells of the liquid I_2+Te system were measured at temperatures 250—600°C. Cells with a vapor path were used, together with those in which a vapor transport was forbidden. The difference due to these types of cells was found in the values of not the initial thermoelectric powers but the steady-state ones for only solutions with low Te compositions. In the I_2-rich region, the mechanism is discussed by using the model of charge-transfer due to I_3^- as in the case of conductivities and absorption spectra. The thermoelectric data in both the Te-rich and intermediate composition regions suggest that electronic contributions are highly predominant and a transition to delocalized states continuously appears with increasing Te concentration. Some experiments were carried out in order to examine the formation of concentration gradient due to the thermal effect in low Te compositions.

In this paper we report measurements of thermoelectric powers on the molten I_2+Te system, for which the conductivity measurements[1] have been made over the entire composition range. For the measurements cells in which a vapor transport was completely forbidden and those in which it was slightly permitted were used. The effect of vapor transport is negligible usually for the initial thermoelectric power measured before the concentration gradient due to thermal effects is formed. However, it is important for the stationary-state thermoelectric power of a system containing highly volatile components, as demonstrated in the case of molten Bi+$BiBr_3$ solutions by Kelner *et al.*[2] The data we obtained (with or without a vapor shunt) also indicate a marked difference in the stationary-state values in the region of low Te compositions, but no difference in the other regions. Experiments were carried out in order to examine the transport number of electron in the TeI_4 liquid and the formation of the concentration gradient in the low Te composition range.

The conductivity data[1] suggest that this system shows a transition from ionic transport to electronic transport; in the I_2-rich region the electrical conduction can be determined largely by the migration of the I_3^- ion, the presence of which could be confirmed by absorption spectra,[3] and by the movement of electron in the Te-rich and intermediate concentration region. The thermoelectric data are discussed by means of the same mechanisms, together with formulas[4] based upon thermodynamics of irreversible process.

Experimental

Materials. The purity of the tellurium and iodine used was described previously.[3]

Apparatus and Procedure. (i) Thermoelectric power: Measurements were carried out with three different thermocells. The Hario thermocell (cell A) with a gas shunt was of the same type as described.[5] For cell A′, all the upper surface of the solution was kept in equilibrium with a gaseous phase across the desired small temperature difference. The horizontal cell (cell B) of J-type, was designed in such a manner that no vapor path between the electrodes was permitted.

The initial thermoelectric power θ_{in} was determined from the slope of a curve of cell emf plotted against ΔT in the range 0.5°—5°. The measurements were carried out at 2 min intervals. In the case of stationary-state thermoelectric power θ_{st} all the emf values were checked to be constant by the recorder. The thermoelectric powers were measured at temperatures 300—550°C and for the compositions 3, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, and 100 at.% Te in I_2.

(ii) Electronic transport number: Wagner's polarization technique[6,7] was used to determine the electronic transport numbers of molten TeI_4. A constant current (0.1—0.3 mA) supplied by an automatic current regulator was passed through the cell, represented by

$$\mathrm{W}|\mathrm{Te(S)}|\mathrm{TeI_4(L)}|\mathrm{C}|\mathrm{W},$$

where W denotes a tungsten lead, Te(S) a solid tellurium cathode and C a graphite rod. The stoichiometric TeI_4 liquid prepared from the samples crystallized by Bridgman's method was enclosed in a capillary with length 60 mm and inner diameter 0.5 mm. The potential applied was so low that the decomposition of the TeI_4 melt could be avoided.

Results

The thermocell used in this work can be regarded as a symmetrical cell W|I_2+Te|W.[5] The temperature effects on θ_{st} for the I_2+Te solutions are shown in Figs. 1—4. For the iodine solutions containing 30, 40, 50 at.% Te, the magnitude and temperature dependence of θ_{st} measured with cells A and A′ differ significantly from those measured with cell B. On the other hand, no difference was found in the values of θ_{in} for the three types of thermocells. In Fig. 5 θ_{in} and θ_{st} (measured with cell B), are plotted against the Te concentrations, giving minima at about 50 at.% Te. Figure 6 shows that the difference between the initial and stationary values, $\Delta(\equiv\theta_{\mathrm{in}}-\theta_{\mathrm{st}})$, reaches a maximum at about 30 at.% Te composition, and continuously approaches zero with increasing Te concentration.

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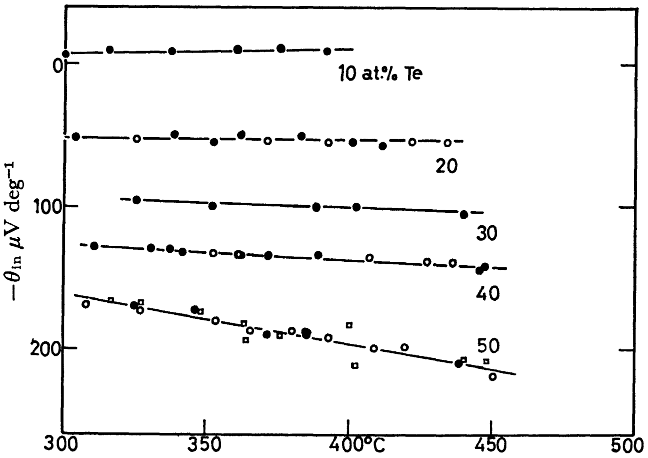

Fig. 1. Initial thermoelectric power θ_{in} (μV/deg) (●, ○, and □, measured with the thermocells A, B, and A′, respectively).

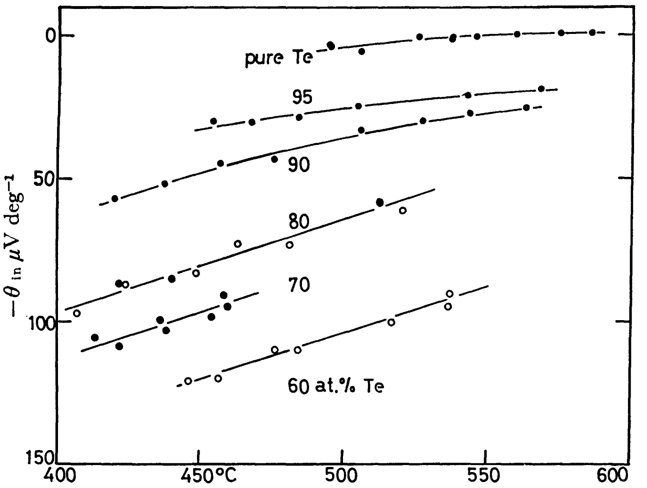

Fig. 2. Initial thermoelectric power θ_{in} (μV/deg) (● and ○, measured with the thermocells A and B, respectively).

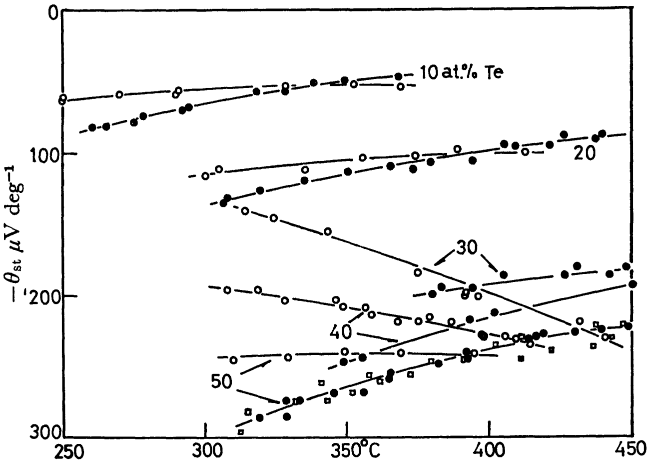

Fig. 3. Stationary-state thermoelectric power θ_{st} (μV/deg) (●, ○, and □, measured with the thermocells A, B, and A′, respectively).

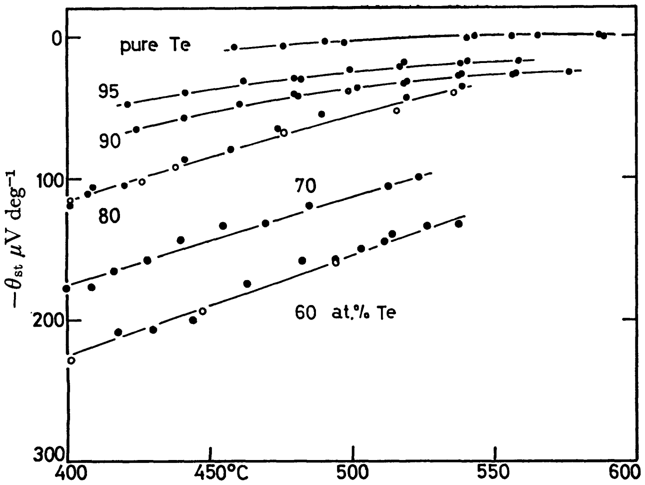

Fig. 4. Stationary-state thermoelectric power θ_{st} (μV/deg) (● and ○, measured with the thermocells A and B, respectively).

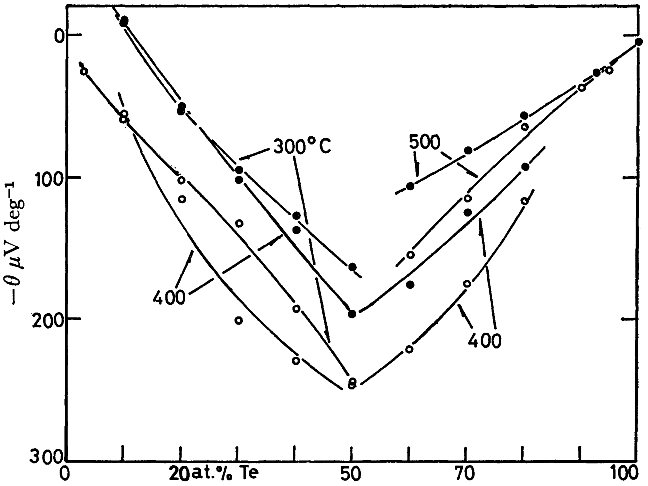

Fig. 5. Initial and stationary-state thermoelectric powers θ_{in}(≡ ●) and θ_{st}(≡ ○) (μV/deg), measured with the thermocell B, as a function of compositions.

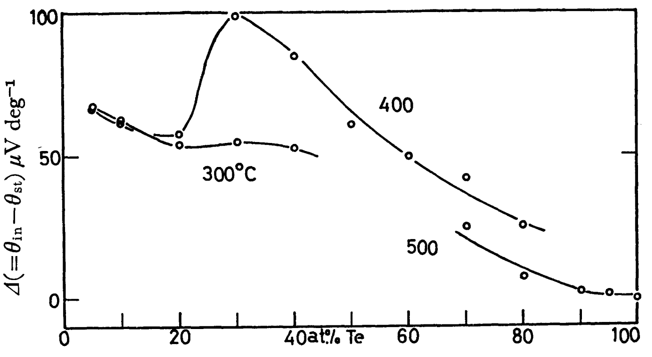

Fig. 6. Dependence of difference $\Delta(=\theta_{in}-\theta_{st})$ (μV/deg) on composition, obtained with the thermocell B.

The electronic transport number t_e in the TeI_4 liquids varies from 0.03 to 0.08 at 300—350°C.

Discussion

The stationary-state data obtained using cells A and A′ seem inadequate for discussing uniquely the thermoelectric powers of the some iodine solutions (*i.e.*, 30, 40, 50 at.% Te), since in these cells with gas shunts the effect of mass transport (mainly due to the I_2 molecule), taking place simultaneously through the gaseous space, is too large to be neglected. Thus, we confine our attention to the results of thermoelectric powers to which no gaseous transport contributes.

As has been pointed out in our conductivity work, the electrical properties of the present system should be examined with three kinds of models applied to the solutions of limited composition ranges.

Charge–Transfer due to I_3^-. In the I_2-rich region (above 95 at.% I), where the contribution of the I_3^- ion to the electrical conduction is predominant, the thermoelectric power θ can be represented by[5]

$$\theta = \theta(\text{hom}) + \theta(\text{het}) + Q. \qquad (1)$$

Here, the homogeneous contribution θ (hom) arising from thermal diffusion of the I_3^- ion is approximately given by

$$\theta(\text{hom}) = [\text{grad}\,\mu(I_3^-)]_T/e\,\text{grad}\,T + q^{**}(I_3^-)/eT, \qquad (2)$$

where the notation is the same as in our previous paper[5] (except for $q^{**}(k)$ in place of $Q^{**}(k)$). Heterogeneous contribution of the solution θ (het) can be written using the entropy factors of electron arising from some chemical reaction at the surface of electrodes (as proposed for the case of a contact between a solid electrolyte and inert electrodes[8]), and Q represents the absolute thermoelectric power of metal leads. The factor containing $[\text{grad}\,\mu(i)]_T$ is zero for the initial state. Thus we get

$$\theta_{\text{in}}(\text{hom}) = q^{**}(I_3^-)/eT. \qquad (3)$$

For the stationary state the concentration gradient formed in the melt can be in local equilibrium.

$$\theta_{\text{st}}(\text{hom}) = [h_V(I_3^-) + q^{**}(I_3^-)]/eT, \qquad (4)$$

where $h_V(I_3^-)$ is the heat of formation for the I_3^- ion.

The application of the Fokker-Planck equation to the thermoelectric phenomena predicts[5,8,9] that the heat of transport is equal to the heat of activation for migration. Inferring from the temperature dependence of mobilities of I_3^-, we can estimate the value of $q^{**}(I_3^-)$ to be 0.12 eV.[1] The value of $h_V(I_3^-)$, which may be equivalent to $-eT\Delta$ with the condition that the heterogeneous value is unchanged in both cases, is found to be negative as seen in Fig. 6. This fact $[h_V(I_3^-)<0]$ is reasonably expected also in our works on the conductivities[1] and the absorption spectra[3] for these compositions. The negative value of θ (het) (*e.g.*, at 300°C for 5 at.% Te θ (het) $= -192\ \mu\text{V deg}^{-1}$) is sufficiently probable in the case of inert electrodes. As an example, θ (het) for molten $PbCl_2$ in contact with graphite, tungsten or platinum electrodes was estimated[10] to be negative (their average value of about $-300\ \mu\text{V deg}^{-1}$), with the aid of data obtained from cells with reversible electrodes.

Electronic Conduction. Case I, Te-rich Region: We showed that the 90 at.% Te solution may be on the borderline of the hopping conduction,[1] and the transition to nonlocalized states may continously appear with increasing Te concentration. As seen in Fig. 6, above the 90 at.% Te composition Δ is negligible within experimental error, and the electronic transport number can be exepcted to be nearly equal to unity. Thus, the total thermopower can be given by

$$\theta = -Q(\text{sample}) + Q(\text{leads}), \qquad (5)$$

with the absolute thermoelectric power Q(sample) of the solutions

$$Q(\text{sample}) = -(\pi^2 k_B^2 T/3e)[\partial \ln \kappa_e(\varepsilon)/\partial\varepsilon]_{\varepsilon=\varepsilon_F}, \qquad (6)$$

where the notation is the same as in our previous paper.[5] According to Mott,[11] for some disordered structures a minimum or pseudogap is expected in the curve of the density of states $N(\varepsilon)$. If the Fermi energy ε_F has a chance of being located at the side lower than the minimum, then the positive values of Q(sample) will be obtained. On the other hand, a negative Hall effect may be expected as in the case of the pure Te liquid.[12] This contradicts the conclusion of the conventional band model. No conduction electrons in liquid Te can, however, be interpreted in terms of a localized model due to Tièche and Zareba.[12] It is well-known[13] that the sign of thermoelectric power in many electron-conducting liquids is not always in agreement with that of the Hall coefficient, although no satisfactory theoretical interpretations have been proposed.

Electronic Conduction. Case II, Intermediate composition region: In the 60—80 at.% Te solutions, conductivity κ varies from 1 to 300 $\text{ohm}^{-1}\cdot\text{cm}^{-1}$ and $\text{d}\kappa/\text{d}T>0$. The transport number of electron t_e is considerably small in the TeI_4 liquid. The magnitude of ionic conductivity in the 20—40 at.% Te solutions can be regarded as nearly constant (*i.e.* 0.4 $\text{ohm}^{-1}\cdot\text{cm}^{-1}$ from the conductivity data at 300—400°C). The rapid increase in κ above the 60 at.% solutions should mainly be interpreted in terms of some electron transport mechanism. In other words, the electron-pair exchnage between the ionicpairs (*e.g.* Te^{2+}, Te^{4+}, Te^{6+} etc.) may be responsible for the electrical conduction under conditions where the composition fluncuations in their environments bring the ions to a level of equal energy.[5]

For the homogeneous part of thermoelectric power at the initial state we can write

$$\theta_{\text{in}}(\text{hom}) = q^{**}(2e)/2eT \qquad (7)$$

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and for that at the stationary state

$$\theta_{st}(\mathrm{hom}) = [h_V(2e)+q^{**}(2e)]/2eT, \qquad (8)$$

which are analogous to Eqs. (3) and (4). Here, $h_V(2e)$ is the heat needed to form the site containing the electron-pair, and $q^{**}(2e)$ the heat of transport of the electron-pair. As in Case I, the value of $h_V(2e)$ can be estimated by the experimental data of Δ. Thus we have $h_V(2e) = -0.03$ eV at 70 at.% Te and at 500°C. No magnitude of $q^{**}(2e)$ can, however, be evaluated only from the data of the thermoelectric powers, since the temperature dependence of the heterogeneous part might be so large that it masks that of the homogeneous part. The heterogenous quantity of the solution can be considered to have a configurational entropy term[14] involving permutation of electron pairs among available states such as $\mathrm{Te}^{(n-2)+}$ and Te^{n}, the concentrations of which might depend significantly on temperature. On the other hand, the value of $q^{**}(2e)$, using the Fokker-Planck equation from the slope $(\Delta h_s+\Delta h^*)$ of $\log(\kappa_e T)$ *vs.* $1/T$ (see Eq. (15) in Ref. (5a)), can be estimated to be 0.33 eV at 70 at.% Te and 500°C.

Formation of concentration gradient In the course of time t the concentration gradient, resulting from the term of $[\mathrm{grad}\ \mu(i)]_T/\mathrm{grad}\ T$ in the expression such as Eq. (2) for the species i, is represented by[4,15]

$$\mathrm{grad}\, c_i = (\mathrm{grad}\, c_i)_\infty[1-\exp(-t/\Theta_i)], \qquad (10)$$

$$\Theta_i = l^2/\pi^2 D_i$$

in which $(\mathrm{grad}\ c_i)_\infty$ denotes the concentration gradient in the stationary state, Θ_i a characteristic time, l the length of diffusing species taking in the cell, and D_i the interdiffusing coefficients. Equation (10) states that the time needed to reach the stationary state becomes longer as l becomes longer. For example, in this work it was observed that the time required for attainment of stationary state in the cells (cell B) with l=32 and 59 mm, containing the 30 at.% Te solution, is 20 and 65 (—95) min, respectively, after the temperature difference across the cell was kept constant.

Formation of the concentration gradient in cell B also can be confirmed also by observing the absorption spectra, characteristic to some species, for the quenching samples. For instance, the I_2 solution containing 30 at.% Te, which had been in the stationary state under conditions where the temperature difference ΔT is 15° at the average temperature 298°C, was rapidly quenched at the liquid nitrogen temperature, and cut into three parts, corresponding to the cool (C), average (A) and hot (H) regions. The absorption spectra of these parts, measured with a diffuse reflectance method, show an increase in relative peak intensity arising from the existence of the I_3^- ion[3] in the order (C), (A), and (H) (or numerically 1 : 1.14 : 1.36).

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