BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1104—1109 (1968)

Electric Conductance and Density of Molten Salt Systems: $I_2 + SbI_3$, $SbBr_3 + SbI_3$, and $SbCl_3$

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(Received December 4, 1967)

Measurements of electric conductance as a function of temperature have been made for the pure liquids; I_2, $SbCl_3$, $SbBr_3$ and SbI_3, and the mixtures; I_2+SbI_3 and $SbBr_3+SbI_3$, from 100 to 250°C. Furthermore, measurements of density by a pycnometric method as a function of temperature have also been made for these mixtures, from 100 to 300°C. The conductivities of these liquids lie in the range from 5×10^{-4} to 1×10^{-5} ohm^{-1} cm^{-1}, and are about 10^{-4} times lower than those of alkali halide melts. In these poorly-conducting pure liquids, the molecules may be considered as constituting a solvent in which slightly dissociated ions are contained. The negative temperature coefficient of conductivity for iodine is in marked contrast to the antimony halide melts, and may be interpreted in terms of the ionic conduction and electron hopping mechanism rather than the metallic one.

A few measurements concerning the electric conductance of pure molten iodine and antimony halides (or group VA metals) have been reported so far,[1-4] and some discrepancies in experimental data have been found. Furthermore, no full datum has been obtained for the electric conductance of mixtures of these antimony halides. The present communication reports the experimental results of density measurements for I_2+SbI_3 and $SbBr_3+SbI_3$ solutions, and of conductivity measurements for I_2+SbI_3, $SbBr_3+SbI_3$ and $SbCl_3$. The measurement of the conductivity of I_2+SbI_3 was made in order to investigate the change in transport properties of an iodine melt due to the addition of antimony iodide. This system is in striking contrast to the molten antimony+antimony halide mixture reported in an earlier paper.[5]

1) I_2: G. N. Lewis and P. Wheeler, *Z. Physik. Chem.*, **56**, 179 (1906); M. Rabinowitsch, *ibid.*, **119**, 83 (1926); W. A. Plotnikov, J. A. Fialkov and W. P. Tschalij, *ibid.*, **A172**, 307 (1935); D. J. Bearcroft and N. H. Nachtrieb, *J. Phys. Chem.*, **71**, 316 (1967).

2) $SbCl_3$: P. Walden, *Z. Anorg. Allgem. Chem.*, **25**, 219 (1900); Z. Klemensiewicz, *Bull. Acad. Cracow*, **487** (1908); G. Jander and K. H. Swart, *Z. Anorg. Allgem. Chem.*, **299**, 252 (1959).

3) $SbBr_3$: V. A. Izbekow and V. A. Plotnikow, *Z. Anorg. Allgem. Chem.*, **71**, 336 (1911); G. Hevesy, *Medd. Danske Selsk.*, **3**, 20 (1921); G. Jander and J. Weis, *Ber. Bunsenges. Physik. Chem.*, **61**, 1275 (1957).

4) SbI_3: G. Hevesy, *Medd. Danske Selsk.*, **3**, 17 (1921).

Experimental

Materials. Guaranteed reagent-grade $SbBr_3$ and $SbCl_3$ were dried under vacuum to remove surface and some hydrated water. All samples (guaranteed reagent-grade I_2, SbI_3, $SbBr_3$ and $SbCl_3$) were purified once or twice by distillation or sublimation *in vacuo*.

Apparatus and Procedure. Conductivity measurements were made with a Jones bridge,[6] constructed of the grounding circuit and measuring one. Alternating current was detected by a "tuned" null detector. The pyrex conductance cell[5] previously described was used with some modification. In particular, the sample of $SbCl_3$, distilled twice *in vacuo*, was directly distilled into the conductance cell through an extension tube, in order to prevent an apparent conductivity due to traces of moisture, and the cell was then sealed off under vacuum. Good precision was obtained by adjusting a variable condenser (0.45—0.70 μF) connected in parallel with the standard resistor. A pyconometric method[7] was used to measure the densities of liquid I_2+SbI_3 and $SbBr_3+SbI_3$ mixtures as a function of temperature and composition. The height of the liquid column was measured with a cathetometer within ±0.005 cm. In order to prevent condensation on the stem wall above the liquid, the top of the stem, which was fitted with a heating coil,

5) K. Ichikawa and M. Shimoji, *Trans. Faraday Soc.*, **62**, 3543 (1966).

6) G. Jones and R. C. Josephs, *J. Am. Chem. Soc.*, **50**, 1049 (1928).

7) F. J. Keneshea, Jr. and D. Cubicciotti, *J. Phys. Chem.*, **62**, 843 (1958).

was maintained at a temperature slightly higher (from 3 to 4°C) than the liquid temperature. The Archimedean method may be unsuitable because of the change in composition due to the appreciable vapour pressures of the samples of interest.

Results and Discussion

The specific conductance κ and the density d_t of I_2+SbI_3 and $SbBr_3+SbI_3$, and κ of $SbCl_3$ were measured over a temperature range from 100 to 350°C above their liquidus temperatures. The temperature dependence of conductivity for each system is shown in Figs. 1, 2 and 3. Table 1 shows the linear relations for the density of the mixtures I_2+SbI_3 and $SbBr_3+SbI_3$. The experimental values (I_2; 3.727 g/cc at 170°C, $SbBr_3$; 3.260 at 200°C) obtained for pure I_2 and $SbBr_3$ are somewhat smaller than those (I_2; 3.796 at 170, $SbBr_3$; 3.416 at 200) of Billet,[8]

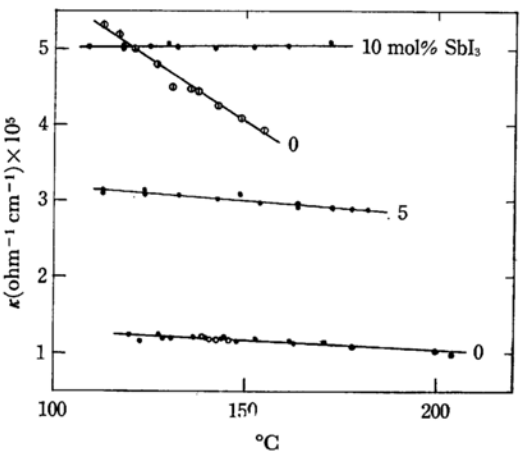

Fig. 1. Conductivity of I_2+SbI_3 solutions against temperature at various mol% SbI_3 compositions. ●, This work; ○, Bearcroft and Nachtrieb[1]; ◐, Rabinowitsch[1]

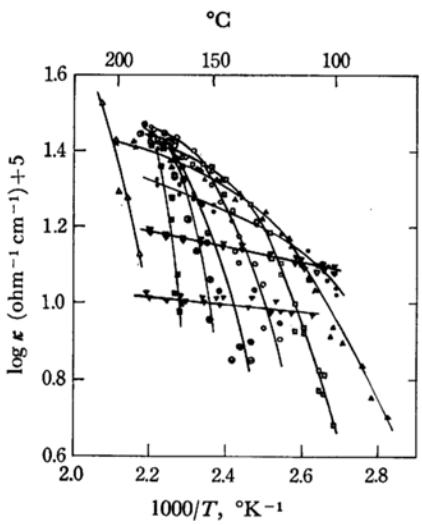

Fig. 2. Log conductivity of I_2+SbI_3 solutions against reciprocal temperature at various mole% SbI_3 compositions (▼: 20, ▽: 30, ●: 40, ▲: 50, □: 60, ○: 70, ⊖: 80, ⊙: 90, ◪: 95, △: 100 mol% SbI_3).

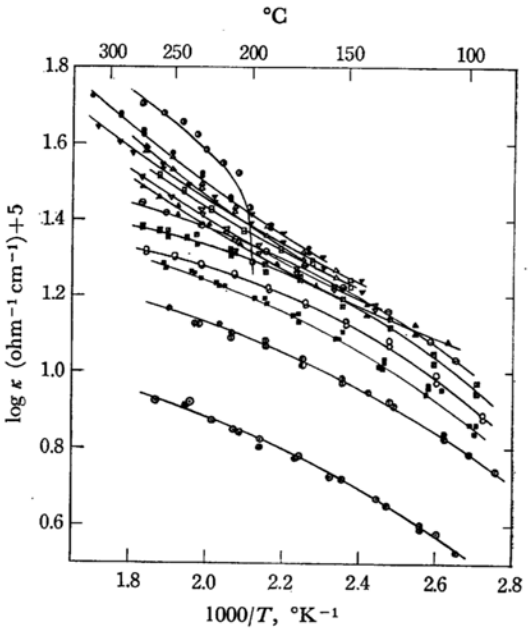

Fig. 3. Log conductivity of $SbBr_3+SbI_3$ solutions against reciprocal temperature at various mol% SbI_3 compositions (⊙: 0, ◐: 5, ■: 10, ○: 20, ◪: 30, ⊖: 40, ▲: 50, ▽: 60, □: 70, ▼: 80, △: 90, ●: 95, ◑: 100 mole% SbI_3).

TABLE 1. DENSITY EQUATIONS FOR I_2+SbI_3 AND $SbBr_3+SbI_3$ MIXTURES

(A) I_2+SbI_3

Mole fraction SbI_3	$d_t=a-bt$ (g/cc) a	$b\times10^3$	Standard error g/cc	Exptl. temp. range, °C
0.000	4.203	2.797	0.042	118—184
0.200	4.190	2.490	0.063	99—226
0.400	4.176	2.205	0.053	113—222
0.600	4.376	2.433	0.027	137—192
0.800	4.423	2.160	0.067	97—235
1.000	4.588	2.483	0.073	182—322

(B) $SbBr_3+SbI_3$

Mole fraction SbI_3	$d_t=a-bt$ (g/cc) a	$b\times10^3$	Standard error g/cc	Exptl. temp. range, °C
0.000	3.762	2.510	0.080	100—256
0.200	3.888	2.152	0.074	106—281
0.400	4.078	2.568	0.091	94—280
0.600	4.208	2.377	0.102	93—280
0.800	4.373	2.490	0.079	153—285
1.000	4.588	2.483	0.073	182—322

8) F. Billet, *L'Institute*, **23**, 292 (1855).

TABLE 2. TEMPERATURE DEPENDENCE OF SPECIFIC AND MOLAR CONDUCTANCES OF LIQUIDS I_2, $SbCl_3$, $SbBr_3$ AND SbI_3

I_2			$SbCl_3$			$SbBr_3$			SbI_3		
t°C	$10^5\kappa$	$10^4\Lambda$	t°C	$10^5\kappa$	$10^3\Lambda$[a]	t°C	$10^5\kappa$	$10^3\Lambda$	t°C	$10^4\kappa$	$10^2\Lambda$
120	1.23	8.07	76	0.770	0.655	104	3.36	3.47	209	3.40	4.20
128	1.22	8.05	79	2.52	2.15	111	3.81	3.95	218	3.59	4.46
137	1.21	8.04	92	5.07	4.38	118	3.96	4.13	228	3.90	4.87
140	1.19	7.95	118	6.46	5.71	131	4.55	4.79	230	3.95	4.94
153	1.18	7.93	134	7.29	6.53	136	4.62	4.88	233	4.16	5.21
162	1.16	7.87	156	8.34	7.62	153	5.26	5.63	235	4.24	5.32
171	1.14	7.77	177	9.31	8.68	154	5.31	5.69	241	4.44	5.59
178	1.08	7.40	195	10.1	9.57	174	5.94	6.46	244	4.52	5.70
200	1.02	7.10	215	10.7	10.3	193	6.63	7.32	252	4.63	5.87
204	0.96	6.73	231	11.3	11.1	205	6.95	7.74	259	4.84	6.17
						209	7.07	7.90	264	4.90	6.26
						222	7.46	8.41	271	5.03	6.46
						240	8.19	9.37			
						261	8.34	9.71			

a) Density data[18]

TABLE 3. EXPONENTIAL EQUATION FOR CONDUCTIVITY OF I_2+SbI_3 AND $SbBr_3+SbI_3$ MIXTURE

(A) I_2+SbI_3

Mole fraction SbI_3	$\kappa = \exp\left(\frac{-B}{T-T_0} - CT + E\right)$
0.200	$\kappa = \exp\{-86.4/(T-146)-8.89\}$
0.300	$\kappa = \exp\{-183/(T-152)-8.18\}$
0.400	$\kappa = \exp\{-461/(T-159)-6.90\}$
0.500	$\kappa = \exp\{-216/(T-165)-2.30\times10^{-2}T+9.66\}$
0.600	$\kappa = \exp\{-3839/(T-171)-4.606\times10^{-2}T+26.33\}$
0.700	$\kappa = \exp\{-6448/(T-178)-9.212\times10^{-2}T+56.79\}$
0.800	$\kappa = \exp\{-7370/(T-184)-9.212\times10^{-2}T+60.94\}$
0.900	$\kappa = \exp\{-6377/(T-190)-9.212\times10^{-2}T+57.46\}$
1.000	$\kappa = \exp\{-614.9/(T-197)-5.83\}$

(B) $SbBr_3+SbI_3$

Mole fraction SbI_3	$\kappa = \exp\left(\frac{-B}{T-T_0} - CT + E\right)$
0.000	$\kappa = \exp\{-640/(T-161)-2.07\times10^{-3}T-6.56\}$
0.050	$\kappa = \exp\{-575/(T-163)-1.61\times10^{-3}T-6.40\}$
0.100	$\kappa = \exp\{-633/(T-165)-2.30\times10^{-3}T-5.60\}$
0.200	$\kappa = \exp\{-758/(T-168)-4.61\times10^{-3}T-3.96\}$
0.300	$\kappa = \exp\{-576/(T-172)-2.30\times10^{-3}T-5.53\}$
0.400	$\kappa = \exp\{-500/(T-175)-1.15\times10^{-3}T-6.20\}$
0.500	$\kappa = \exp\{-438/(T-179)-6.93\}$
0.600	$\kappa = \exp\{-461/(T-182)-6.84\}$
0.700	$\kappa = \exp\{-474/(T-186)-6.68\}$
0.800	$\kappa = \exp\{-532/(T-190)-6.40\}$
0.900	$\kappa = \exp\{-532/(T-193)-6.36\}$
0.950	$\kappa = \exp\{-647/(T-195)-5.92\}$
1.000	$\kappa = \exp\{-615/(T-197)-5.83\}$

18) D. I. Juraflef, *Zh. Fiz. Khim.*, 13, (1939).

and Jander and Weis.[8] Table 2 shows the temperature dependence of the molar conductance Λ (or the product $\Lambda = \kappa V$ of the specific conductance κ and molar volume V) as well as κ for the pure melts I_2, $SbCl_3$, $SbBr_3$ and SbI_3. The specific conductance may be represented by the exponential function,

$$\kappa = \exp\left(\frac{-B}{T-T_0} - CT + E\right) \qquad (1)$$

which is almost similar to the equation due to Yaffe and Artsdalen,[9] though another expression which is a quadratic function[10] of temperature has often been employed. Two parameters (C and T_0) and two constants (B and E) in Eq. (1) are given in Table 3.

(A) **Conductivities for Pure Melts.** In poorly-conducting melts; I_2, $SbCl_3$, $SbBr_3$ and SbI_3, the molecules may be considered as constituting a solvent medium in which slightly dissociated ions (often univalent ions) exist, and with which they are in dynamic equilibrium with respect to the process of ionization. According to Jander *et al.*,[2,3] the fused $SbCl_3$ and $SbBr_3$ are regarded as a "waterlike ionizing solvent" for a considerable number of organic and inorganic compounds, especially for covalent ones. These melts may therefore be expected to obey Walden's rule[11] ($\Lambda\eta$=constant, with η the viscosity) to the extent to which the conditions for Stokes' law[12] holds. An estimate of the degree of dissociation, α, of the electrolytes which obey Walden's rule is possible using Greenwood and Martin's equation,[13]

$$\alpha = \frac{\Lambda\eta}{100}. \qquad (2)$$

From the values (see Table 4) calculated from Eq. (2), it may be seen that these pure melts are slightly dissociated, by about 5×10^{-3} per cent.

TABLE 4. DEGREE OF DISSOCIATION α OF SOME MOLTEN SALT, SUCH AS $SbCl_3$, $SbBr_3$ AND I_2

Salt	t°C	$10^3\,\Lambda$ ohm^{-1} cm^2 mol^{-1}	η cp	$10^5\,\alpha$
$SbCl_3$	150	7.06	1.01	7.1
$SbBr_3$	150	5.05	1.20	6.1
I_2	150	0.747	1.80	1.3

$SbCl_3$: viscosity data[19]
$SbBr_3$: viscosity data[19]
I_2 : viscosity data[20]

i) I_2 (see Table 2 and Fig. 1). Published values[1] for the conductivity of pure liquid iodine range from 0.092 to 1.68×10^{-4}ohm^{-1}cm^{-1} at 140°C. As seen in Fig. 1, our conductivity data for pure liquid iodine are in good agreement with the data of Bearcroft and Nachtrieb[1] (their work was presented shortly after our measurements had been completed, and their measurements were limited to the temperature range of 139—146°C). However, there exist large discrepancies between the above data and those reported by Rabinowitsch,[1] and it is of interest that the values for the I_2+10 mol% SbI_3 system in our work are similar to those of the I_2 melt of Rabinowitsch at 121°C (see Fig. 1). It is found to have negative temperature coefficient, or $d\kappa/dT = -3.1\times10^{-8}$ ohm^{-1} cm^{-1} deg^{-1} (-4.3×10^{-8}, Bearcroft and Nachtrieb, and -2.2×10^{-7}, Rabinowitsch). It is uncertain whether the conduction phenomena may be interpreted (Rabinowitsch[1]) in terms of the metallic conduction mechanism only, in view of the negative temperature coefficient obtained for the conductivities. It is desirable to investigate other transport properties, such as the Hall effect. Riggleman and Drickamer[14] proposed that a discontinuity in the slope of the resistance-pressure curve at 235 K bar represented the beginning of metallic conduction for solid iodine. The decrease in interatomic distance due to high pressure may bring about the transition from ionic conduction to metallic conduction. On the other hand, another point of view is that electron hopping occurs, as well as ionic conduction. Liquid iodine may consist of a neutral species nI_2 with I^-_{2n-1} and I^+ ions, through the reaction (Bearcroft and Nachtrieb[1])

$$nI_2 \rightleftarrows I^+ + I^-_{2n-1} \qquad (3)$$

just as in aqueous solution. As shown in Table 4, the degree of dissociation α of liquid I_2 is small, about one fifth of that of the antimony halide melts. It is well known that the ionization constant in aqueous solutions of some weak electrolytes often has a maximum at a particular temperature; that is to say, the heat content change on the ionization of weak electrolytes is often negative at high temperatures.[15] Then, it is of interest to examine whether or not an analogous result is obtained in liquid iodine containing partially auto-dissociated ions. The temperature dependence of the number density n_j, given by $n_j \propto \exp(-\Delta H_j/2RT)$, can be calculated from Eq. (3) for the chemical reaction (particularly for $n=1$), and from Greenwood and Martin's Eq. (2). Figure 4 shows that the calculated heat content change on ionization ΔH_j is negative and nearly independent of temperature in this temperature range (about -5.7 kcal·mol^{-1}). For such a slightly dissociated molecular melt, the temperature dependence of the

9) I. S. Yaffe and E. R. Artsdalen, *J. Phys. Chem.*, **60**, 1125 (1956).
10) See, *e.g.*, L. A. King and F. R. Duke, *J. Electrochem. Soc.*, **111**, 712 (1964).
11) P. Walden, *Z. Physik. Chem.*, **A157**, 389 (1931).
12) A. Einstein, *Ann. Physik*, **4**, 549 (1905).
13) N. N. Greenwood and R. L. Martin, *J. Chem. Soc.*, **1953**, 1427.
19) A. J. Batschinski, *Z. Physik. Chem.*, **84**, 643 (1913).
20) "Inter. Critic. Tables," Vol. VII, McGraw-Hill Comp., New York (1933), p. 212.
14) B. M. Riggleman and H. G. Drickamer, *J. Chem. Phys.*, **37**, 446 (1962).
15) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Pub., London (1959), p. 336.

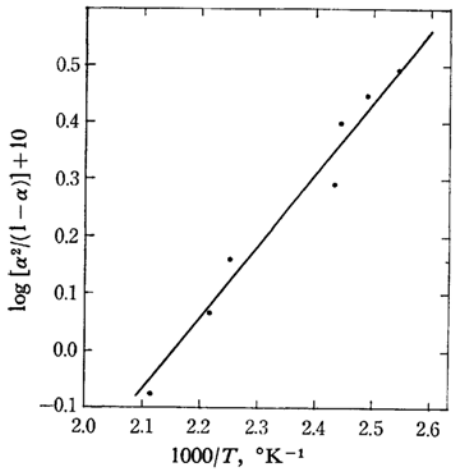

Fig. 4. Log $\alpha^2/(1-\alpha)$ as a function of reciprocal temperature for pure I_2 melt.

carrier concentration may be appreciable compared with that of the mobility due to ionic migration as well as electron hopping. For example, the negative temperature dependence for conductivities of HgI_2 have been interpreted in terms of such an ionic conduction mechanism.[16] Bearcroft and Nachtrieb[1] have recently proposed that I^- is transferred from I^-_{2n-1} ions to neighbouring I_2 molecules, and the mobility of I^- is large compared with that of I^+. It is to be noted that the surface self-diffusion coefficient D^* of species I^- for both mono- and multilayers of I_2 adsorbed on metals in the temperature range 145—235°C has an order of magnitude of 10^{-6} cm^2 sec^{-1} according to Arnikar and Mehta.[17] This charge transfer may also be interpreted in terms of the electron hopping mechanism proposed here.

ii) *$SbCl_3$* (see Table 2). According to previous papers,[2] the conductivity of pure $SbCl_3$ melt has been found to vary from 0.85×10^{-6} to 1.69×10^{-4} ohm^{-1} cm^{-1} immediately above the melting point, though it was not investigated as a function of temperature. Our experimental results (see Table 2), obtained as a function of temperature, lie in the mid-point of the above data. Jander and Swart[2] has proposed that electric conduction results from the self-dissociation reaction

$$SbCl_3 \rightleftarrows xSbCl_2^+ + xCl^-\cdot(1-x)SbCl_3\,, \quad (4)$$

where $xCl^-\cdot(1-x)SbCl_3$ refers to xCl^- ion solvated by $(1-x)SbCl_3$ molecules. The observed conductivity κ is put equal to the sum of each conductivity. According to our formula for ionic conductivity,[5] the mobility μ_i of the ionic species i is

$$\mu_i \simeq (d_i^2\nu_i Z_i e/kT)\exp[-B_i/(T-T_{0i}) - \Delta h_i/kT] \quad (5)$$

In view of the size and mass of each species contributing to the conductivity, the mobility of $SbCl_2^+$ may be much larger compared with that of $xCl^-(1-x)\cdot SbCl_3$. It seems that the condudctivity κ may be nearly equal to $\kappa_{SbCl_2^+}$.

iii) *$SbBr_3$* (see Table 2). The specific conductance of molten $SbBr_3$ obtained in our investigation is smaller by about one tenth, compared with the data

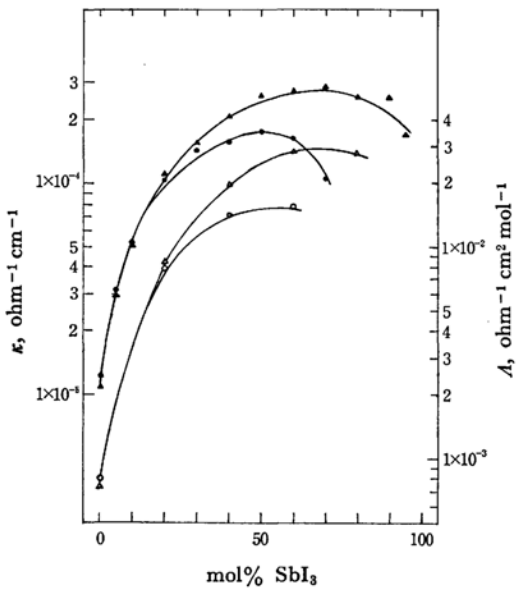

Fig. 5. Specific (● and ▲) and molar (○ and △) conductances of I_2+SbI_3 solutions (▲ and △ at 445°K, ● and ○ at 400).

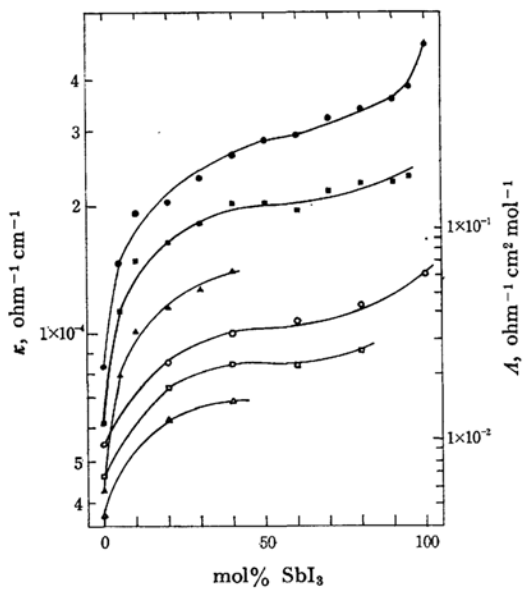

Fig. 6. Specific (●, ■ and ▲) and molar (○, □ and △) conductances of $SbBr_3+SbI_3$ solutions (● and ○ at 525°K, ■ and □ at 455, ▲ and △ at 400).

16) G. J. Janz and J. D. E. Mclutyre, *J. Electrochem. Soc.*, **109**, 842 (1962).
17) H. J. Arnikar and O. P. Mehta, *J. Phys. Chem. Solids*, **24**, 1633 (1963).

due to Hevesy,[3] in the range from 100 to 200°C. The values of κ due to Izbekow and Plotnikow,[3] and due to Jander and Weis[3] were respectively 2.25×10^{-5}, and 1.0×10^{-5} $ohm^{-1}cm^{-1}$ at 100°C, though the temperature dependence of the conductivity was not observed by them. According to Jander and Weis,[3] slight dissociation should be considered, as for pure $SbCl_3$. Then, the species which contributes to the electric conduction may be chiefly $SbBr_2^+$, that is, $\kappa \simeq \kappa_{SbBr_2^+}$.

iv) *SbI_3* (see Table 2). The conductivities of molten SbI_3 are, within experimental accuracy, in agreement with those due to Hevesy.[4] The degree of self-dissociation in pure SbI_3 may be larger, by about ten times, relative to that for pure $SbCl_3$ or $SbBr_3$ in view of the difference between the conductivities of SbI_3, and those of $SbCl_3$ or $SbBr_3$.

(B) Conductivities for Mixtures of Molten Salts.

i) *I_2+SbI_3*. The composition variations in the specific and molar conductances Λ for I_2+SbI_3 are given in Fig. 5. It is of interest that the conductivities increase steeply within the region from 0 to 40 mol% SbI_3 as SbI_3 is added. This may be due to the dissociation of the dissolved SbI_3, as for aqueous electrolytes. With further increase in SbI_3 content, the value of κ has a weak maximum, and then falls monotonically.

ii) *$SbBr_3+SbI_3$*. The composition dependence of κ and Λ for $SbBr_3+SbI_3$ is shown in Fig. 6. The values of κ increase steeply over the range from 0 to 10 mol% SbI_3, because of the dissociation of SbI_3, as for the I_2+SbI_3 solution. With further increase in SbI_3 content, the value of κ increases monotonically.

For poorly-conducting melts, such as I_2+SbI_3, $SbBr_3+SbI_3$ and $SbCl_3$, which are only slightly dissociated, the degree of ionization is an important factor in analyzing the temperature dependence of the conductivities. Then the pre-exponential factor A_i, involved in Eq. (A11) in the previous paper due to Ichikawa and Shimoji,[5] should be regarded as the temperature dependent function since the value of A_i is proportional to the number density n_i of the ionic species i contributing to the conductivity.