The Effect of Pressure on the Electrical Conductivity of the Molten Halides of Mercury and the Molten Iodides of Cadmium, Gallium and Indium

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Dedicated to Professor Alfred Klemm on the occasion of his 70th birthday

The electrical conductivities of molten $HgCl_2$, $HgBr_2$, HgI_2, CdI_2, GaI_3 and InI_3 were measured to pressures of 1 GPa (10 kbar), using a heated pressure vessel pressurised with argon. Additionally, the conductivities of CdI_2 and $HgCl_2$ were measured from 2 to 6 GPa, using a tetrahedral anvil apparatus. In every case the conductivity rose with pressure initially, and this is thought to be due to an increase in the degree of self-ionisation of the liquid. For CdI_2 and HgI_2 a maximum was observed in the conductivity isotherm below 1 GPa, and for $HgCl_2$ the conductivity fell with pressure from 2 to 6 GPa, implying that a maximum exists between 1 and 2 GPa. At the maximum the degree of ionisation approaches unity, and there is a balance between the competing effects of pressure in increasing the degree of ionisation and in reducing the ionic mobilities.

Introduction

In previous publications we have reported isothermal measurements of the electrical conductivity of the mercuric halides [1], and of some group B metal iodides [2] in the pressure range 0 – 100 MPa. Similar work has been reported by other groups [3 – 6]. Pressure influences the conductivity of these liquids in three ways:

(i) if the degree of ionisation were constant, compression of the liquid would be accompanied by an increase in the ionic concentration, and hence the conductivity, in inverse proportion to the volume;

(ii) the degree of self-ionisation changes with pressure, which leads to a corresponding change in the conductivity;

(iii) the relative ionic mobilities vary with pressure.

Effect (i) is generally relatively small, and can be calculated directly from the compressibility. For fully ionised liquids such as the alkali halides [7] and nitrates [8 – 13] effect (ii) is absent and effect (iii) predominates. At temperatures close to the melting point the mobilities usually fall with pressure, so a reduction in conductivity is observed. For slightly self-ionised liquids effect (ii) outweighs (iii) in the pressure region up to 100 MPa; increasing self-ionisation with pressure causes a conductivity increase which more than offsets any reduction due to changes in ionic mobility. As the pressure is raised further and the degree of ionisation approaches unity, it is to be expected that effect (ii) would be reduced in importance and effect (iii) would eventually predominate. The general expectation is that, over an extended pressure range, the conductivity of partially ionised liquids such as the B-group halides would rise steeply with pressure at first; the rate of rise would be reduced as the degree of ionisation increased, and a maximum would occur where effects (ii) and (iii) balance. Such a maximum has been reported for molten $BiCl_3$ [14]. It is the aim of the present work to study the conductivity of a representative group of liquids showing incomplete self-ionisation at atmospheric pressure, over a pressure range 0 – 1 GPa, in which substantial changes in degree of ionisation may be expected. The anticipated maximum in the conductivity isotherms was observed for CdI_2 at 0.65 GPa and 781 K, and for HgI_2 at 0.95 GPa and 823 K. Some further work was carried out on CdI_2 and $HgCl_2$ using a tetrahedral press, in the pressure range 2 – 6 GPa. The conductivities of both compounds fell with pressure in this range, implying that a conductivity maximum must exist for $HgCl_2$ between 1 and 2 GPa.

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Experimental

Materials

The compounds chosen for this study were $HgCl_2$, $HgBr_2$, HgI_2, CdI_2, GaI_3 and InI_3. The mercuric halides were melted and filtered through porosity 4 Pyrex frits to remove particulate impurities. They were than equilibrated with the corresponding halogen to oxidise any mercurous compounds present; the chloride and iodide were sublimed in the gaseous halogen, and the bromide was left in refluxing bromine for 24 h. Finally, each compound was sublimed twice *in vacuo* and stored in a dry atmosphere until required. GaI_3 and InI_3 were prepared by direct combination of the elements. The metals (99.9999%, Johnson, Matthey & Co.) were refluxed in iodine for one hour, after which excess iodine was removed by boiling. The products were filtered in the molten state, and sublimed twice *in vacuo*. Subsequent exposure to the atmosphere was avoided. CdI_2 was recrystallised twice from triply distilled water.

High Pressure Apparatus and Experimental Procedure (0 – 1 GPa)

A pressure vessel capable of working in the range 0 – 1 GPa and 20 – 600 °C was designed and constructed. The vessel body was made from a creep-resisting alloy REX 559 (Firth Brown Ltd., Sheffield, England) with end flanges of EN 25 and closure screws of EN 27 (Hadfields Ltd., Sheffield). The screws held in position hardened steel plugs of ORVAR 2 (Uddeholm, Stockholm); one of these had a central hole through which pressurised gas entered the vessel, and the other carried four insulated electrical leads allowing conductivity and temperature measurements to be made inside the vessel. The central section of the pressure vessel was heated externally using mineral-insulated heaters (Pyrotenax Ltd., Hebburn-on-Tyne) wound non-inductively on the body of the vessel and lagged with Kaowool insulating felt (Carborundum Co. Ltd.). The spacing between the coils of the heater was adjusted to give an isothermal zone of length 60 mm in the centre of the vessel. The end flanges of the vessel were water cooled to maintain the pressure seals at room temperature. A diagram of the vessel and one of the plugs is shwon in Figure 1. Figure 2 shows the layout of the apparatus. The vessel, pressure intensifier (Harwood Engineering Co., type A25J), pressure transducer (Astra Corporation, Hatboro, Penn.) and associated valves and pipework (Pressure Products Inc., Hatboro) were housed in a steel cubicle in a room which was kept locked when the apparatus was under pressure. The handles of the valves and all wires from the heaters, transducer and pressure vessel passed through a brick wall into the adjoining laboratory where the operator was situated. Before use in these experiments the vessel was tested and autofrettaged by pressurising it to 1.1 GPa at room temperature using isopropanol as pressurising fluid. In subsequent use of the vessel the pressure was never raised above 1.0 GPa.

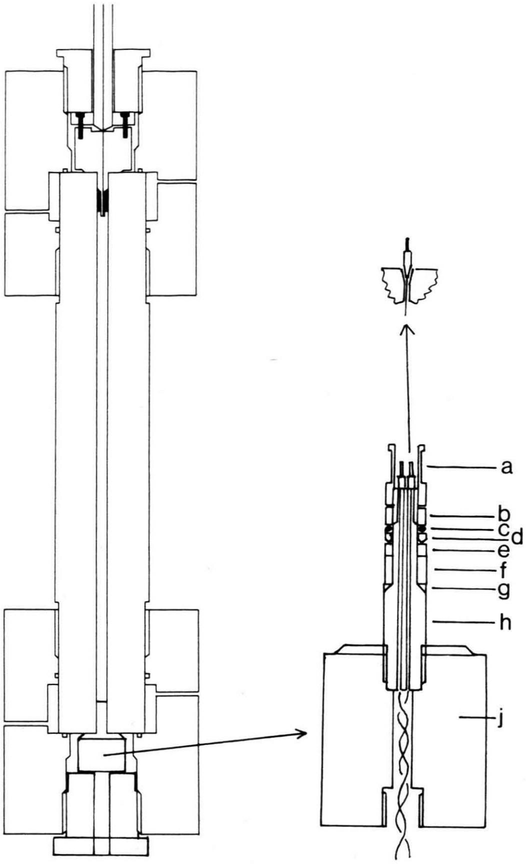

Fig. 1. The pressure vessel used in the range 0 – 1 GPa. The closure plug and sealing rings are shown in detail: a) bayonet fitting for attatchment of stainless steel guard tube; b) retaining collar; c) rubber O-ring; d) bronze ring; e) lead ring; f) leather ring; g) bronze anti-extrusion ring; h, j) stem and body of plug, made from ORVAR 2. The initial seal is made by the rubber ring c, and the sealing function passes successively to components e and f as the pressure is raised.

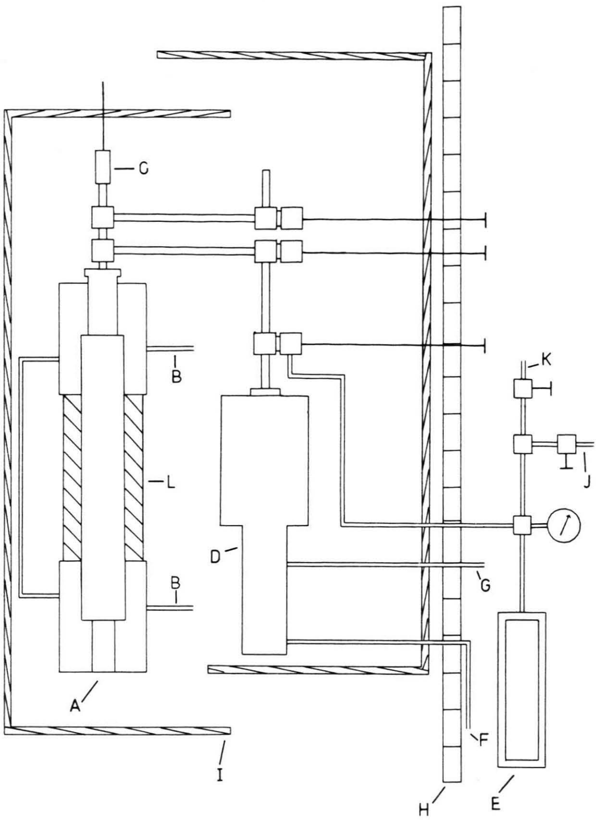

Fig. 2. Schematic layout of 1 GPa rig (not to scale). A) pressure vessel (see Fig. 1); B) water cooling to end flanges; C) pressure transducer; D) intensifier; E) pressure reservoir for storage of argon at 0.1 GPa; F) hydraulic fluid inlet to low pressure side of intensifier; G) tube filled with coloured liquid, indicating position of intensifier piston; H) brick wall between adjacent laboratories, separating apparatus from operator; I) enclosure made from 5 mm mild steel plate and lined with 18 mm soft-board; J) argon inlet from compressor; K) outlet, vented through window; L) furnace and lagging on pressure vessel.

The temperature inside the heated zone of the pressure vessel was measured with a chromel-alumel thermocouple connected to two of the insulated terminals in the closure plug of the vessel. The conductivity cell was connected to the other two terminals. Two types of cell were used (see Fig. 3); one had a Pyrex capillary between the electrodes, and had a cell constant of the order $10^4\ \mathrm{m}^{-1}$, and the other had electrodes much nearer together in the 'rod and ring' configuration, with a cell constant of the order $100\ \mathrm{m}^{-1}$. In each case, the part of the cell containing the electrodes was fused to the end of a commercial hypodermic syringe. Cell constants were determined at 25 °C using 0.01 or 0.1 Demal KCl solution [15]. The electrodes were made from platinum for the work on the mercuric halides, and from tungsten for the remaining compounds. The 'rod and ring' cell was used only for the work on mercuric chloride, which has a lower conductivity than the other compounds. Cells were filled in a glove box under a dry argon atmosphere. The compound to be studied was fused into the cell, and the solid glass piston was inserted until it made contact with the molten compound. The cell contents were then allowed to freeze, teflon tape was wound around the exposed part of the piston and the cell was connected to the terminals of the closure plug of the pressure vessel by platinum leads. The teflon tape was removed, and a guard tube of stainless steel was placed over the cell and thermocouple. This tube extended over the full length of the bore of the pressure vessel; its function was to prevent contact between the vessel wall and any corrosive vapours which might escape from the cell during the experiment. Corrosion of the vessel wall would damage the smooth finish, and could initiate failure. The free space inside the guard tube on either side of the cell was filled with lengths of ceramic rod, to reduce convection currents in the pressurising gas and also to reduce the quantity of

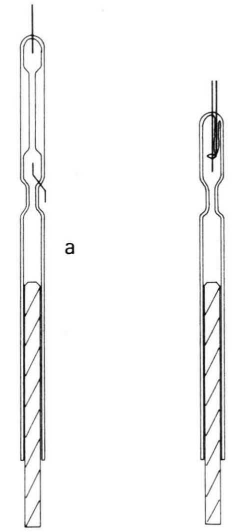

Fig. 3. Conductivity cells: a) capillary type, with cell constant of the order $10^4\ \mathrm{m}^{-1}$; b) 'rod and ring' type, with cell constant of the order $100\ \mathrm{m}^{-1}$. The lower part of each cell is made from a hypodermic syringe, with solid, ground-glass plunger.

gas required to raise the apparatus to a given pressure.

The pressure vessel was preheated to the desired working temperature, with the cooling water flowing through the end flanges to prevent possible overheating of the seals. A safety cut-out was incorporated into the heater circuit, such that accidental interruption of the water flow caused the power supply to the heater to be switched off. The plug, guard tube and cell were inserted as a single unit, and the plug was pushed into its working position by tightening the backing screw. External connections were made, and the room was cleared of personnel and locked. The conductivity was measured at atmospheric pressure for each compound at a temperature fairly near the melting point. Comparisons were made with literature values, as a check on sample purity. The pressure was then raised to about 0.1 GPa, and the temperature was increased by some 200 K. This was done to ensure that the sample would still be liquid when the pressure was subsequently raised to 1 GPa, it being known that melting points generally rise with pressure by some 10 – 20 K per 100 MPa.

Conductance measurements were made [1] as a function of increasing pressure, 30 minutes being allowed for temperature restabilisation after each pressure change. The pressurising gas was argon, taken from commercial cylinders at ca. 10 MPa, compressed to 100 MPa by a diaphragm compressor [1] and further compressed to the working pressure by the intensifier. The function of the glass piston in the conductivity cell was to reduce the rate of ingress of dissolved argon into the liquid between the electrodes to an acceptably low level. On normal operation the piston would slide in smoothly as the pressure was raised, so transmitting the gas pressure to the experimental liquid. Occasionally the piston would seize, in which case erratic readings would be obtained. Attempts were made to take readings as the pressure was reduced from the maximum value. These attempts were rarely successful; seizure of the glass piston almost always occurred, possibly because gas was being evolved from solution in the thin layer of working liquid between the piston and the barrel of the syringe. When the piston seized, fracture of the cell usually occurred soon afterwards.

Measurements were made on molten $HgCl_2$, $HgBr_2$ and HgI_2 to 1 GPa, on CdI_2 and InI_3 to 0.8 GPa and on GaI_3 to 0.6 GPa. Maxima were observed for HgI_2 and for CdI_2, but for the other compounds the conductivity was still rising at the highest pressure used. It was decided to attempt experiments in a higher pressure range in order to search for conductivity maxima for these compounds.

High Pressure Experiments to 6 GPa

The apparatus used for these experiments was a tetrahedral press situated at Standard Telecommunications Laboratories, Harlow, Essex [16, 17]. A miniature conductivity cell was incorporated into the pyrophyllite tetrahedron which acts as the pressure transmitting medium in this apparatus. A cross-section through the tetrahedron is illustrated in Figure 4. The cell was made from alumina tubing, with electrodes consisting of platinum beads pushed into each end. The cell was packed in MgO powder, surrounded by a mica sleeve and finally by a tantalum tube, whose ends extended outwards to the surfaces of the tetrahedron. The cell was retained inside the tantalum tube by packing the open ends with a mixture of MgO and epoxy resin. A thermocouple was inserted through a hole drilled from the centre of one edge of the tetrahedron. The assembly was placed between the four anvils of the press, the thermocouple and the insulated platinum leads from the cell being brought out between adjacent pairs of anvils. The two anvils which contacted the ends of the tantalum tube could be connected to a low-voltage welding transformer; a current of about 300 A then passed through the tube, and its temperature could be raised to over 900 K.

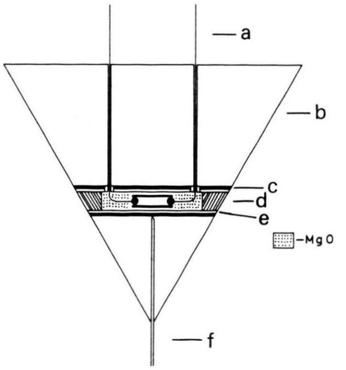

Fig. 4. Section through pyrophyllite tetrahedron used in tetrahedral anvil, showing detail of conductivity cell and furnace. The edge length of the tetrahedron was 20 mm. a) conductance leads; b) pyrophyllite; c) tantalum tube heater; d) MgO/epoxy resin mixture; e) mica sleeve; f) stainless-steel-sheathed thermocouple.

Measurements were made on CdI_2 and on $HgCl_2$. The cell was filled with the powdered compound, compacted as tightly as possible, and was mounted in the press assembly as described above. If the power to the tantalum heater was turned on while the cell was still at atmospheric pressure, it was found that the salt melted and ran out of the cell. In order to avoid this problem it was necessary to load the ram and compact the pyrophyllite tetrahedron while the cell contents were still solid. The compound then remained in the cell when the heating current was applied. The ram thrust required to achieve this initial sealing corresponded to a sample pressure of 2 GPa, which is therefore the lower pressure limit for these experiments. Since the previous experiments had an upper limit of 1 GPa, the range 1 – 2 GPa was not accessible. Experiments were carried out on CdI_2 to 6.5 GPa, and on $HgCl_2$ to 4.5 GPa.

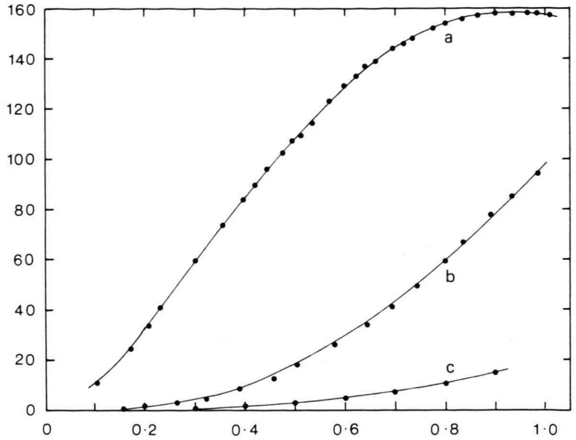

Fig. 5. Conductivity isotherms for molten mercuric halides to 1 GPa. a) HgI_2 at 823 K; b) $HgBr_2$ at 772 K; c) $HgCl_2$ at 573 K. Ordinate: Conductivity/(Sm^{-1}); Abscissa: Pressure/(GPa).

Results

The conductivity isotherms up to 1 GPa were fitted to a polynomial:

$$\log_{10}(\text{conductivity}/\text{Sm}^{-1}) = a + b\,P + c\,P^2 + d\,P^3 + e\,P^4 + f\,P^5$$

with P in GPa, using a non-linear least squares program EO2ACF from the NAGS library. The values of the coefficients are listed in Table 1. The conductivity isotherms are presented graphically in Figs. 5 and 6. The results obtained for CdI_2 and $HgCl_2$ at pressures above 2 GPa are shown in Fig. 7, together with the data from the lower pressure range. Maxima in the conductivity isotherms were found, as follows:

CdI_2: 0.63 GPa at 781 K,

HgI_2: 0.95 GPa at 823 K,

$HgCl_2$: between 1 and 2 GPa at ca. 800 K.

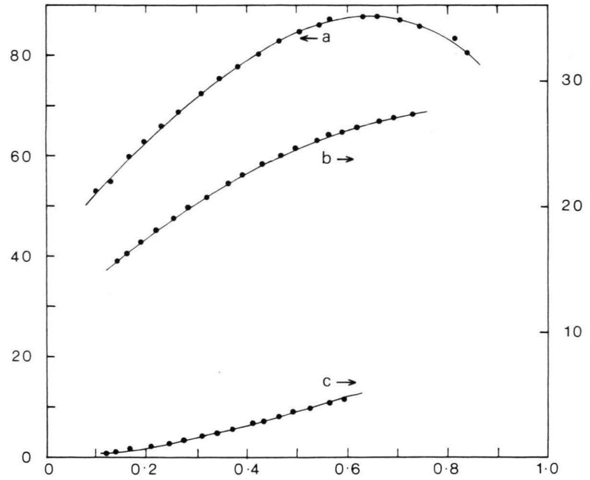

Fig. 6. Conductivity isotherms for molten iodides to 1 GPa. a) CdI_2 at 781 K; b) InI_3 at 674 K; c) GaI_3 at 676 K. Ordinate: Conductivity/(Sm^{-1}); Abscissa: Pressure/(GPa).

Table 1. Coefficients of polynomial equations giving $\log_{10}$ (conductivity/Sm^{-1}) as a function of pressure/GPa in the ranges indicated.

Compound	Pressure Range/GPa	Temperature/K	a	b(GPa^{-1})	c/(GPa^{-2})	d/(GPa^{-3})	e/(GPa^{-4})	f/(GPa^{-5})
$HgCl_2$	0.1 – 0.9	773	– 1.912	7.901	– 13.022	22.340	– 24.056	10.202
$HgBr_2$	0.1 – 1.0	772	– 1.247	10.285	– 20.899	30.871	– 24.898	7.851
HgI_2	0.1 – 1.0	823	0.152	11.011	– 28.551	40.947	– 30.051	8.684
CdI_2	0.1 – 0.85	781	1.654	0.645	1.162	– 5.136	6.209	– 2.762
GaI_3	0.1 – 0.6	676	– 2.663	33.761	– 182.710	522.189	– 725.235	386.754
InI_3	0.15 – 0.75	674	1.009	1.742	– 3.886	6.062	– 5.398	1.929

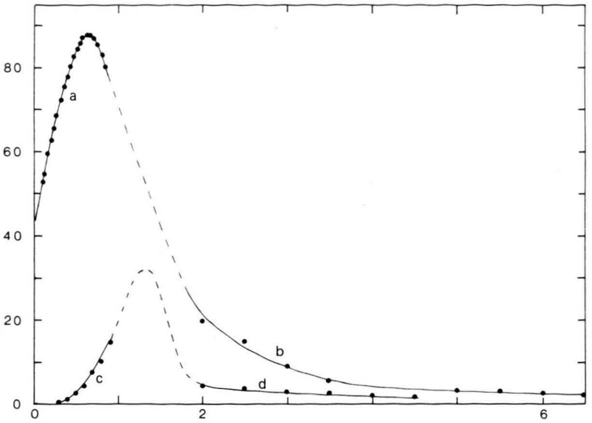

Fig. 7. Combined results over extended pressure range for CdI_2 (a) 773 K, b) 823 K) and $HgCl_2$ (c) 773 K, d) 823 K). Ordinate: Conductivity/(Sm^{-1}); Abscissa: Pressure/(GPa).

Discussion

Experimental errors

Cell constants were determined at 25 °C and 1 atm. A simple calculation, based on the expansivity and compressibility of Pyrex, showed that the cell constant would decrease by about 0.2% as the temperature was raised from 25 °C to the working temperature, and would increase by about 1% when the pressure was raised from atmospheric to 1 GPa. No corrections have been applied for these small changes. The conductance bridge was accurate to 0.1%. The uncertainty in the temperature measurement was estimated to be ± 2 K. This includes temperature fluctuations during each run, and an allowance for the effect of pressure on the thermocouple emf [18]. The pressure transducer was calibrated aginst a dead weight tester by the manufacturer. There was no evidence of hysteresis or zero drift, and the accuracy of the pressure measurement is estimated to be ± 0.1%.

For the experiments in the tetrahedral anvil, the pressures were calculated from the ram thrust using calibration data supplied by STL [17]. The calculation of conductivity from the measured conductance is based on the cell constant obtained from the dimensions of the cell at the beginning of the experiment. The cell must have been quite heavily distorted by application of pressure, and the cell "constant" probably rose with pressure. It is difficult to estimate a correction, but the error may be as high as a factor of 2 at the highest pressures. Dissection of the pyrophyllite tetrahedron at the end of an experiment showed the cell to be broken but to have retained its original shape. In view of the uncertainty in the cell constant, the 40 – 50 K difference in temperature between the experiments at 0 – 1 GPa and those at 2 – 6 GPa is of little significance. The higher temperature of 823 K was used in the anvil experiments to prevent freezing of the sample at the higher pressures.

Comparison with Previous Work

As a check on sample purity, the conductivity of each compound was measured at a temperature close to the melting point. For the mercuric halides, agreement with published values [19] was within 1%, and the pressure coefficients of conductivity for these compounds were in similarly good agreement with previous work [1, 4]. Agreement with the literature was also excellent for CdI_2 [19] and for InI_3 [20] at atmospheric pressure. For GaI_3 at 555 K, the conductivity value from this work is 5.38×10^{-2} Sm^{-1}, which compares well with 5.6×10^{-2} from one source [2] but very poorly with 11.7×10^{-2} from another [21]. This discrepancy is presumably due to differences in sample purity, but it is not clear which sample was the purest. The pressure coefficients of conductivity compare rather poorly with our own previous measurements [2]; the present results should take precedence.

Significance of the Results

Conductivity maxima have been found on the conductivity versus pressure isotherms for HgI_2 and CdI_2, and a maximum must exist for $HgCl_2$ in the pressure range 1 – 2 GPa which was not accessible in our experiments. From the shapes of the isotherms for GaI_3, InI_3 and $HgBr_2$, there is every reason to believe that maxima would have been found for these compounds also if the experiments had been extended to higher pressures. In general, the conductivity-pressure isotherms are S-shaped up to the maximum. Plots of log (conductivity) versus pressure (not shown) are concave downwards over the whole pressure range, i.e. the slope of each plot decreases with rising pressure. As a measure of this slope we have calculated the "activation volume", defined empirically by the equation

$$\Delta V_{\varkappa} = - RT(\partial \ln \varkappa / \partial P)_T. \quad (2)$$

Table 2. Values of the "acitvation volume" (cm^3/mol) at rounded values of pressure (see Eq. (2)).

Compound	Temperature/K	Pressure / (GPa)										
		0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$HgCl_2$	773	–	−87.0	−69.3	−58.2	−49.6	−41.3	−33.0	−25.9	−23.5	−30.6	–
$HgBr_2$	772	–	−103	−72.5	−54.9	−44.6	−37.6	−31.4	−24.7	−17.8	−12.3	−11.3
HgI_2	823	–	−101	−56.9	−32.1	−19.6	−13.5	−10.0	−6.7	−2.96	0.3	0.5
CdI_2	781	–	−11.1	−10.0	−7.7	−5.1	−2.9	−1.0	1.1	4.4	10.4	–
GaI_3	676	–	−132	−41.7	−31.9	−27.0	−12.1	−32.3	–	–	–	–
InI_3	674	–	−14.5	−9.8	−7.0	−5.3	−3.9	−2.7	−1.6	–	–	–

Values of this quantity, at rounded values of pressure, are presented in Table 2. The values were obtained by differentiating the polynomial equation (1) and inserting the appropriate coefficients from Table 1. We have refrained from making the calculation at pressures higher than those reached in the experiments; although the polynomials give a good fit to the data within the experimental range, extrapolation of such high order equations would probably yield spurious results.

The results confirm our previous suggestion [2] that the degree of ionisation of incompletely ionised liquids increases with pressure at constant temperature. This is in accordance with Klemm's Rule [22], which asserts that the molar volume of a system in which there is partial covalent bonding between the particles is higher than that of the corresponding ionic system. According to le Chatelier's principle, application of pressure to such a system would favour the formation of the ionic species. Observations of a similar kind to those described here have also been made for the liquid interhalogen compounds ICl, IBr and BrF_3; all show an increase in electrical conductivity with pressure [23].

It is noteworthy that $\Delta V_\varkappa$ is extremely large for GaI_3 and for the halides of mercury. The main term contributing to $\Delta V_\varkappa$ at low pressures for these compounds is the volume change for the ionisation process:

$$2\,HgI_2 \rightleftharpoons HgI_3^- + HgI^+ \text{ (etc.)}.$$

The fact that the volume change for this process is so large implies that the position of the ionisation equilibrium is extremely sensitive to the volume of the system, which can be altered either by applying pressure, as in these experiments, or by changing the temperature at constant (e.g. atmospheric) pressure. This is the reason why the conductivity falls as the temperature is raised for these compounds [20], an effect which is contrary to experience for dilute strong electrolyte solutions or for fully ionised molten salts.

Our work has demonstrated that slightly self-ionised liquids which at low pressure are largely molecular in character can be converted reversibly to ionic liquids by application of pressure. No doubt there would be associated changes in chemical properties accompanying this transition; for example, the gradual loss of Lewis acid character on the part of compounds such as HgI_2 and GaI_3 is to be expected. Changes in colour (i.e. visible and ultra-violet absorbtion spectra) and in vibrational spectra would also be expected. A direct investigation of such effects provides a fascinating challenge for the future. At atmospheric pressure HgI_2 is immiscible with ionic liquids such as $LiNO_3$. This situation also is expected to change as pressure is a lied to the system, since pressure causes the two liquids to become more similar in chemical nature. This effect is currently under investigation in our laboratory.

Acknowledgements

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