

Offprinted from the *Transactions of The Faraday Society*
No. 580, Vol. 67, Part 4, April, 1971

Pressure Dependence of Electrical Conductivity for Fused Mercuric Halides

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Received 1st September, 1970

The electrical conductivities of molten HgCl_2 , HgBr_2 and HgI_2 have been measured over the pressure range 1-1000 bar at temperatures between 260°C and 370°C. In each case the conductivity increased with pressure; at 300°C, the specific conductance "activation volume" $\Delta V_K = -RT(\partial \ln \kappa / \partial P)_T$, was $-50 \text{ cm}^3 \text{ mol}^{-1}$ for HgCl_2 , $-65 \text{ cm}^3 \text{ mol}^{-1}$ for HgBr_2 and $-102 \text{ cm}^3 \text{ mol}^{-1}$ for HgI_2 . These increases in conductivity are attributed to the displacement of ionization equilibria of the type $2\text{HgX}_2 \rightleftharpoons \text{HgX}^+ + \text{HgX}_3^-$ ($X = \text{halogen}$). The Born equation was used to estimate the volume changes associated with ionization, with results in reasonable accord with the experimental values. The pressure required to cause complete ionization is estimated to be in the range 5-10 kbar. For molten HgI_2 , d.c. electrolysis experiments showed that the increase in conductivity with pressure was *not* caused by the onset of electronic conductivity. Although the conductivity at constant pressure decreases with temperature for HgI_2 , and passes through a maximum with rising temperature for HgBr_2 and HgCl_2 , the conductivity at constant density increases with temperature for all three compounds.

Grantham and Yosim¹ have studied the temperature dependence of electrical conductivity for a wide range of metal halides in equilibrium with their vapours. They found that the conductivity usually increased as the temperature was raised from the melting point, but the rate of increase diminished with rising temperature. In some cases the conductivity-temperature curve passed through a maximum, and for mercuric iodide the conductivity decreased with rising temperature over the whole liquid range. In accounting for these results, Grantham and Yosim suggested that the melts contain covalent molecules in equilibrium with ions, the conductivity being proportional to the product of ion mobility and degree of dissociation. The former increased with rising temperature, causing the increase in conductivity generally observed at lower temperatures. However, the degree of dissociation decreased with temperature, giving rise to the conductivity maximum and subsequent decrease. This fall in the degree of dissociation was thought to be principally a consequence of the density change rather than of the temperature change itself, and the authors suggested that the conductivity would always increase with temperature under conditions of constant density. They recognized that measurements involving pressure as an independent variable would be required to confirm this hypothesis.

We report measurements of the pressure dependence of conductivity for molten HgCl_2 , HgBr_2 and HgI_2 , in the range 1-1000 bar and 260-370°C. The conductivity increased with pressure at constant temperature in each case, in contrast to the behaviour of fully ionized salts such as the alkali nitrates.² Using compressibilities and expansivities taken from the literature, the isochoric temperature coefficients of conductivity have been calculated, and are indeed found to be positive, in accordance with the suggestion of Grantham and Yosim.

EXPERIMENTAL

MATERIALS

HgCl_2 (British Drug Houses Ltd., >99.5 %) was distilled five times in an all-glass apparatus. HgBr_2 (B.D.H., 98 %) was distilled three times in all-glass apparatus, sublimed twice in a stream of argon saturated with bromine vapour at 20°C and finally distilled once. HgI_2 (B.D.H., 99 %) was sublimed once in a stream of air. The purified salts were cast into sticks before loading into the conductivity cells.

CONDUCTIVITY MEASUREMENTS ON HgI_2

The conductivity cell illustrated in fig. 1 was made from Pyrex. The cell constant was 209 cm^{-1} , and was determined using 0.01 Demal KCl solution at 25.0°C. The change in cell constant between 25°C and 368°C is about 0.1 %, which is insignificant. The cell constant is not needed for the evaluation of ΔV_K , and has been used only in comparing our results with those of previous workers. The loaded cell was suspended inside a heated pressure vessel; pressure was applied by admitting argon. The vessel, conductance bridge and general procedure have been described elsewhere.² Access of dissolved argon to the central part of the conductivity cell was prevented by providing a long, narrow diffusion path from the exposed surfaces of the melt. The conductance showed no hysteresis when the pressure was cycled isothermally between atmospheric pressure and 1000 bar over a period of 8 h. Temperatures were measured with a stainless steel sheathed, chromel-alumel thermocouple inside the hot vessel, with its junction positioned near the central capillary of the conductivity cell. The temperature was constant to within $\pm 0.25^\circ\text{C}$ for all measurements in a given pressure cycle. A pressure of 1 kbar changes the e.m.f. of a chromel-alumel couple by an amount corresponding to about 0.1°C , which is too small to warrant application of a correction.³

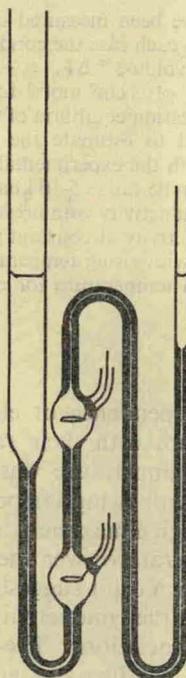


FIG. 1.—Conductivity cell used for HgI_2 .

At the higher temperatures the escape of HgI_2 from the cell by evaporation caused concern, as the vapour corroded the pressure vessel and also condensed in the gas outlet tube, causing blockages. The rate of evaporation was reduced to an acceptable level by placing a 1 cm layer of fused LiNO_3 on the free surfaces of HgI_2 . LiNO_3 and HgI_2 have very similar melting points and form two-phase liquid mixtures with very little mutual solubility.⁴ Some measurements made without the LiNO_3 gave identical results, showing that diffusion of dissolved LiNO_3 into the conduction path was not a significant source of error. Isotherms measured under both conditions are included in fig. 3.

CONDUCTIVITY MEASUREMENTS— HgBr_2 AND HgCl_2

Attempts to measure the conductivity of these compounds in the above apparatus were abandoned, because corrosion of the inside of the pressure vessel and of the stainless steel thermocouple sheath occurred rapidly at 300°C. A new apparatus was designed, in which these difficulties were avoided (see fig. 2). Use was made of a vertically-mounted pressure vessel provided with a heating mantle at the upper end, and a water jacket at the lower end, above the flange closure. The heater was divided into three parts; by adjusting rheostats in parallel with these the temperature gradient in a 3 cm long section was reduced to 0.25°C or less at temperatures and pressures in the range 300–450°C and 1–1000 bar. The conductivity cell was positioned in this isothermal zone, and was covered by a Pyrex tube which was closed at its upper end and which extended downwards into the cold region. Vapour diffusing

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away from the cell condensed on the lower part of the inside wall of this tube, and was thus prevented from reaching the walls of the pressure vessel. The thermocouple and the conductivity cell leads were similarly protected by glass tubes. The conductivity cell contained platinized platinum electrodes of the "ring and rod" type, this configuration being chosen because it makes the cell constant relatively insensitive to dimensional changes in the cell caused by slight distortion during pressure cycling.⁵ Cell constants were about 0.5 cm^{-1} , and were measured before and after each run using 0.01 Demal KCl solution at 25.0°C . The cell constant changed by about 0.3% between room temperature and 330°C (the highest temperature used). Salt was loaded into the cell as a cast stick, and a glass insert placed on top of it. The insert floated on the molten salt, reducing the exposed surface to a narrow annulus. This lowered the rate of evaporation to an acceptable level, and also restricted the rate of diffusion of dissolved gas into the region between the electrodes. No hysteresis in the conductivity was observed during pressure cycles, indicating that gas dissolution did not influence the results significantly.

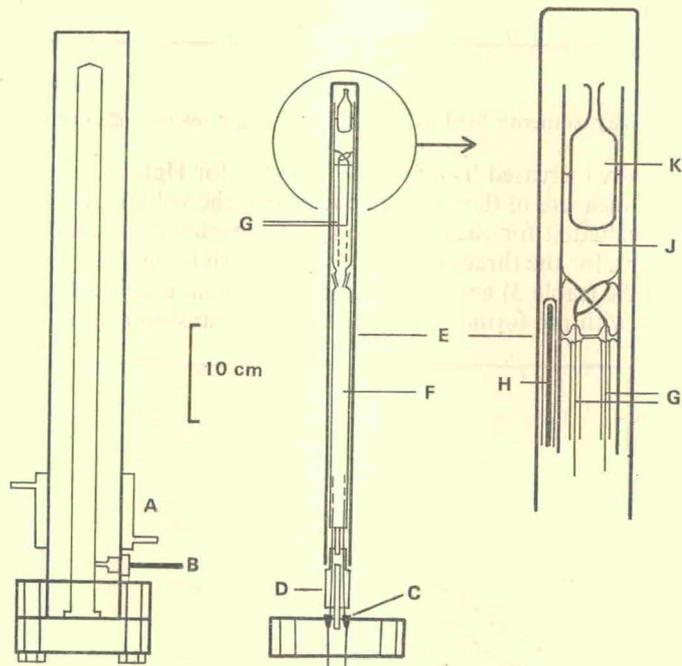


FIG. 2.—Pressure vessel, insert and conductivity cell used for HgCl_2 and HgBr_2 . A, water jacket; B, inlet for high pressure gas; C, Bridgman cones for electrical leads to cell and thermocouple; D, pyrophyllite insulator; E, outer glass tube; F, glass column; G, platinum leads, in glass sheaths; H, stainless steel clad thermocouple, in glass sheath; J, melt; K, glass float.

Conductances were measured with a Wayne-Kerr transformer ratio-arm bridge (type B 221), using an external oscillator (Advance, type J 1) and tuned amplifier null detector (General Radio, type 1232 A). Measurements were made over the frequency range 1 to 10 kHz. Between these limits, the conductivity varied by less than 0.1%. The usual extrapolation to infinite frequency was considered to be unnecessary, in view of the comparatively large changes in conductivity with pressure.

RESULTS

Fig. 3, 4 and 5 show isothermal plots of $\log(\text{conductivity})$ against pressure for HgI_2 , HgBr_2 and HgCl_2 . When the pressure was raised from atmospheric to 1000

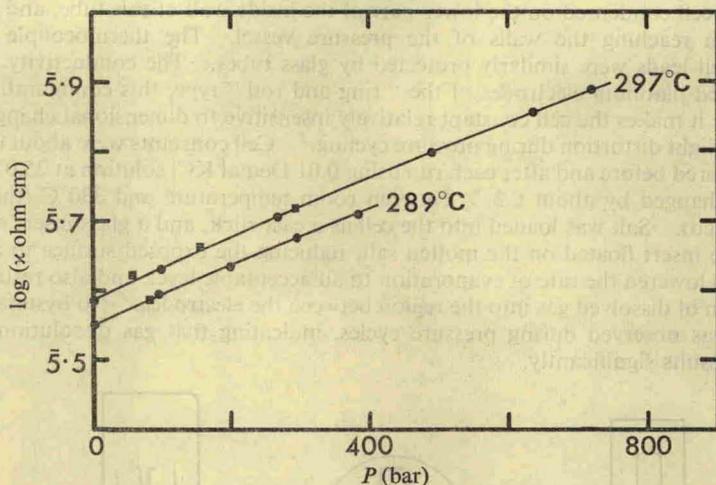


FIG. 3.—Conductivity isotherms for HgCl_2 ; ●, increasing pressure; ■, decreasing pressure.

bar, the conductivity increased by a factor of about 6 for HgI_2 , 3.5 for HgBr_2 and 2.5 for HgCl_2 . As a measure of the pressure coefficient, the volume $\Delta V_\kappa = -RT(\partial \ln \kappa / \partial P)_T$, has been evaluated for each isotherm at atmospheric pressure. Plots of ΔV_κ against temperature for the three compounds are shown in fig. 6. (The symbols ΔV_κ , and later E_p and E_v (table 3) are used in this paper in an empirical sense only; they are not identified with the formation of a particular transition state).

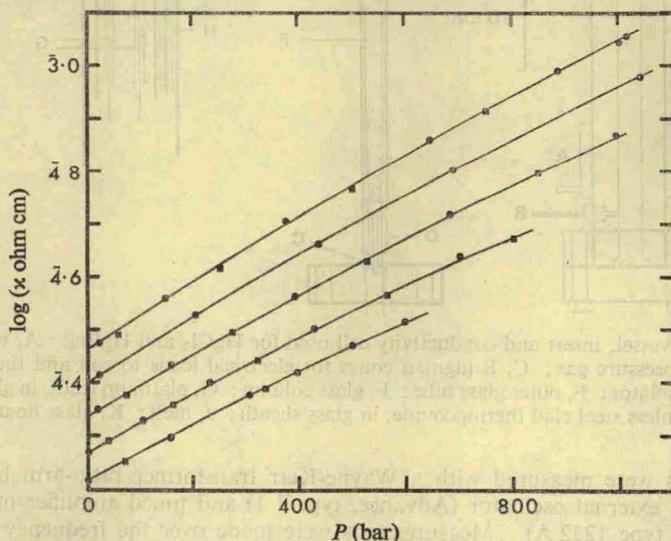


FIG. 4.—Conductivity isotherms for HgBr_2 ; ●, increasing pressure; ■, decreasing pressure. From top to bottom, the temperatures are 331.5, 311, 292.5, 273.5 and 260.5°C.

DISCUSSION

COMPARISON WITH PREVIOUS WORK

The conductivities of the fused mercuric halides have been measured by Grantham and Yosim,¹ Janz and McIntyre⁶ and Bockris *et al.*⁷ Our results for HgI_2 and

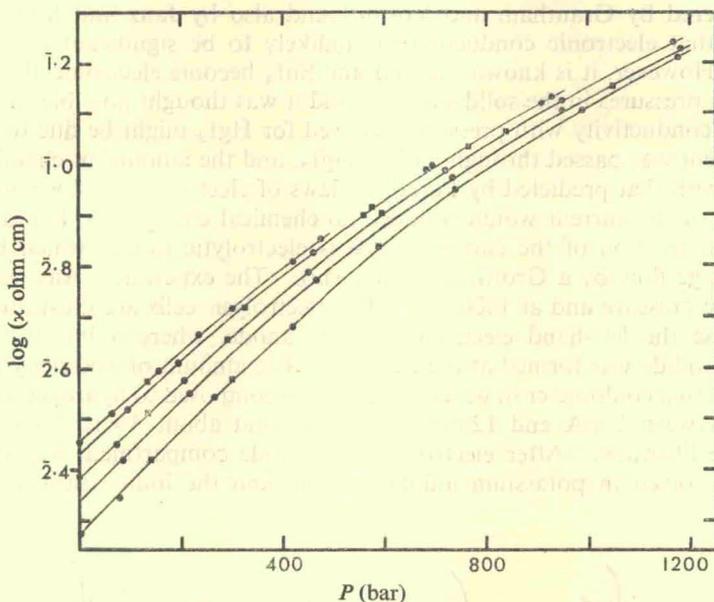


FIG. 5.—Conductivity isotherms for HgI_2 ; ●, increasing pressure; ■, decreasing pressure. From top to bottom, the temperatures are: 276, 287, 310, 332 and 368°C.

HgCl_2 at atmospheric pressure agree with those of ref. 1 and 7 within 1%. For HgBr_2 , our results are about 4% below those of ref. 1, 6 and 7. This small discrepancy may be due to differences in sample purity.

POSSIBILITY OF ELECTRONIC CONDUCTIVITY

Before interpreting these results, we wished to show by experiment whether electronic conductivity contributes significantly to the total conductivity. This point

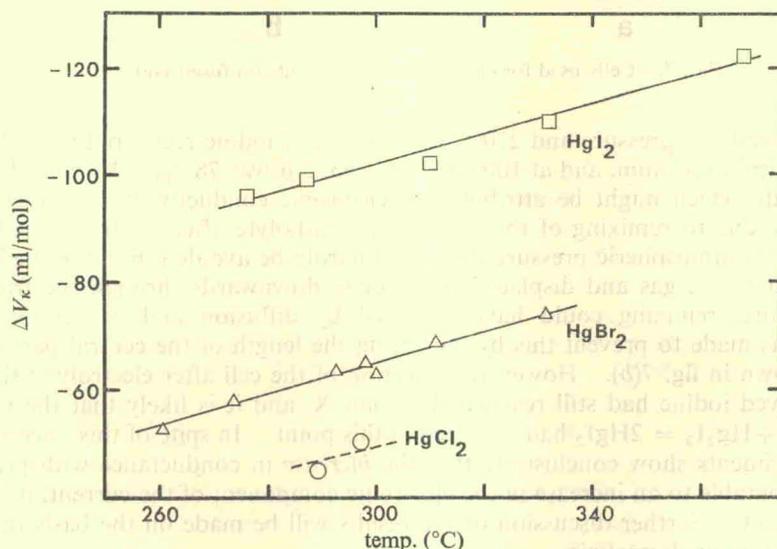


FIG. 6.—Plots of ΔV_{κ} against temperature for the fused mercuric halides.

was considered by Grantham and Yosim,¹ and also by Janz and McIntyre,⁶ who concluded that electronic conductivity is unlikely to be significant at atmospheric pressure. However, it is known that TlI and SnI_4 become electronically conducting at very high pressures in the solid state,^{8, 9} and it was thought possible that the large increase in conductivity with pressure observed for HgI_2 might be due to this cause. Direct current was passed through molten HgI_2 , and the amount of chemical change compared with that predicted by Faraday's laws of electrolysis. Since an electronic component of the current would produce no chemical change, the Faradaic yield is equal to the fraction of the current which is electrolytic (under which heading we include charge flow by a Grotthuss mechanism). The experiment was performed at atmospheric pressure and at 1000 bar. The electrolysis cells are illustrated in fig. 7. In each case the left-hand electrode was the anode, where iodine was liberated. Mercurous iodide was formed at the cathode. The amount of electricity passed was measured with a coulometer in which water was decomposed to hydrogen and oxygen. Currents between 2 mA and 12 mA were used, and about 4×10^{-4} equivalents of iodine were liberated. After electrolysis, the anode compartment was broken, the contents dissolved in potassium iodide solution and the iodine titrated with thio-sulphate.

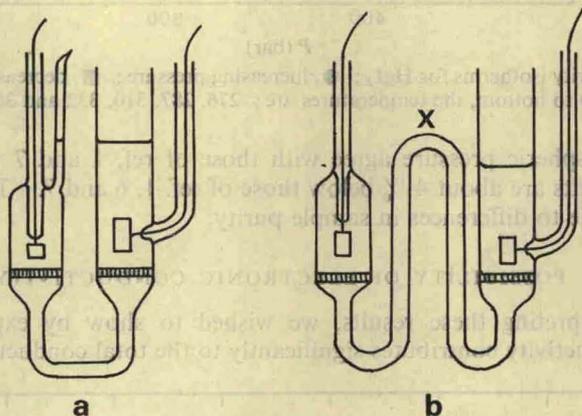
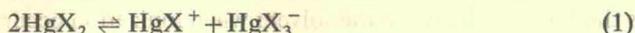


FIG. 7.—Cells used for electrolysis experiments on fused HgI_2 .

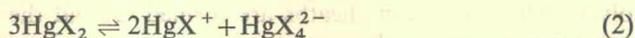
At atmospheric pressure and $270^\circ C$ the amount of iodine recovered was 84 % of the theoretical maximum, and at 1000 bar and $295^\circ C$ it was 78 %. We consider that the shortfall, which might be attributed to electronic conductivity, is in fact more likely to be due to remixing of the anolyte and catholyte after electrolysis. In the experiment at atmospheric pressure this could hardly be avoided, because the iodine was liberated as a gas and displaced the anolyte downwards through the frit. At high pressure, remixing could have occurred by diffusion and convection. An attempt was made to prevent this by increasing the length of the central part of the cell, as shown in fig. 7(b). However, inspection of the cell after electrolysis showed that dissolved iodine had still reached the point X, and it is likely that the reverse reaction $I_2 + Hg_2I_2 = 2HgI_2$ had occurred at this point. In spite of this uncertainty, these experiments show conclusively that the *increase* in conductance with pressure is *not* attributable to an increase in the electronic component of the current, if indeed this is present. Further discussion of the results will be made on the basis that the current is entirely electrolytic.

EFFECT OF PRESSURE ON THE DEGREE OF IONIZATION

Comparison of vapour-phase and liquid-phase Raman spectra shows that, at atmospheric pressure, the fused mercuric halides consist predominantly of linear molecules HgX_2 .^{6, 10-13} The conductivity has been attributed^{1, 6} to slight self-ionization with formation of complex ions



and, to a lesser extent,



The ions HgX^+ , HgX_3^- and HgX_4^{2-} cannot be detected in the pure melts by Raman spectroscopy, but HgX^+ has been found in aqueous solutions of HgX_2 with added $\text{Hg}(\text{ClO}_4)_2$,¹⁴ and spectra due to HgX_3^- , and ultimately HgX_4^{2-} , appear when alkali metal halides are added to molten HgX_2 .^{15, 16} Band intensity data¹⁵ indicate that equilibrium (2) may be ignored in pure HgX_2 melts at atmospheric pressure.

Previous work on fully ionized melts, such as the alkali metal nitrates² or halides,¹⁷ has shown that a pressure of 1000 bar reduces the conductivity by up to 10%. This decrease is attributed to a reduction in the mobilities of the ions, caused by the increase in density. The conductivities of non-aqueous solutions of fully dissociated electrolytes usually decrease with pressure for the same reason.¹⁸⁻²¹ For aqueous solutions of strong electrolytes, increases in conductivity with pressure which are sometimes observed are attributed to changes in solvent structure or to the operation of a Grotthus mechanism, e.g. for proton transfer.⁵ For weak electrolyte solutions, the degree of dissociation increases with pressure, because the solvation of the ions involves a net reduction in the volume of the system.^{22, 23} The same consideration applies to the self-ionization of molecular liquids such as water.²⁴ We now consider whether our results can be accounted for in terms of the displacement of equilibrium (1) to the right with pressure. For this purpose we ignore for the present the effect of pressure on ion mobilities.

Let c denote the concentration, a the activity and f_{\pm} the mean ion activity coefficient of the ions HgX^+ and HgX_3^- . For equilibrium (1),

$$K = a_{\text{HgX}^+} a_{\text{HgX}_3^-} / a_{\text{HgX}_2}^2$$

Since the ionic concentrations are relatively small, we ignore changes in the activity of the molecular species and write

$$K' = a_{\text{HgX}^+} a_{\text{HgX}_3^-} = c^2 f_{\pm}^2$$

Using standard thermodynamics, the change in standard partial molar volume when ionization (1) takes place is given by

$$\overline{\Delta V}^{\circ} = -RT(\partial \ln K' / \partial P)_T = -2RT(\partial \ln c / \partial P)_T - 2RT(\partial \ln f_{\pm} / \partial P)_T \quad (3)$$

Assuming, as a first approximation, that the ion mobilities are independent of pressure at constant temperature,

$$-2RT(\partial \ln c / \partial P)_T \approx -2RT(\partial \ln \kappa / \partial P)_T = 2\Delta V_{\kappa} \quad (4)$$

Comparing eqn (3) and eqn (4), one obtains

$$2\Delta V_{\kappa} = \overline{\Delta V}^{\circ} + 2RT(\partial \ln f_{\pm} / \partial P)_T \quad (5)$$

We now estimate the volume terms on the right side of eqn (5), and compare them with $2\Delta V_{\kappa}$ determined experimentally. $\overline{\Delta V}^{\circ}$ may be considered in two parts

$$\overline{\Delta V}^{\circ} = \overline{\Delta V}_1^{\circ} + \overline{\Delta V}_2^{\circ}$$

$\overline{\Delta V}_1^\circ$ is the volume of the ions HgX^+ and HgX_3^- minus the volume of two HgX_2 molecules, and has been calculated from the appropriate bond lengths and van der Waals radii. The ions HgX_3^- were taken to be planar and trigonal. The van der Waals radii used were ²⁵ (in 10^{-10} m): Hg, 1.25; Cl, 1.80; Br, 1.95; I, 2.15. As table 1 shows, $\overline{\Delta V}_1^\circ$ is less than 1 ml mol^{-1} for all three equilibria, so this contribution to $\overline{\Delta V}^\circ$ is negligible. For the remainder of this section, $\overline{\Delta V}^\circ$ is equated with $\overline{\Delta V}_2^\circ$. $\overline{\Delta V}_2^\circ$ is the volume change in the solvent when ionization occurs, the "solvent" in this case being molecular HgX_2 . $\overline{\Delta V}_2^\circ$ is negative, and represents the electrostriction of the solvent when solvation sheaths are formed around the ions. The standard partial molar free energy of solvation of a spherical ion of charge ze and radius r , in a solvent of permittivity ϵ is given by the Born equation

$$\overline{\Delta G}^\circ = -\frac{Ne^2z^2}{2r} \left(1 - \frac{1}{\epsilon}\right)$$

Differentiating with respect to pressure, we obtain for the standard partial molar volume change on solvation ²⁶

$$\overline{\Delta V}_2^\circ = \left(\frac{\partial \overline{\Delta G}^\circ}{\partial p}\right)_T = \sum_{\text{ions}} \left[\frac{Ne^2z^2}{2r^2} \left(1 - \frac{1}{\epsilon}\right) \left(\frac{\partial r}{\partial p}\right)_T - \frac{Ne^2z^2}{2r\epsilon^2} \left(\frac{\partial \epsilon}{\partial p}\right)_T \right] \quad (6)$$

The terms in the square bracket can be evaluated if ϵ , r and their pressure derivatives are known. For the mercuric halides, experimental values of ϵ are available only for the solids.²⁷ Since the crystals contain non-polar molecules HgX_2 (in the case of HgI_2 , this applies to the yellow modification), ϵ for the liquids can be estimated by assuming that the Clausius-Mosotti function, $V_m(\epsilon-1)/(\epsilon+2)$, undergoes no change when the substance is melted. The density data used were taken from Janz and McIntyre.⁶ Likewise, $(\partial \epsilon / \partial p)_T$ can be found by assuming that the Clausius-Mosotti function is invariant with pressure. The resulting expression for $(\partial \epsilon / \partial p)_T$ is

$$(\partial \epsilon / \partial p)_T = [(\epsilon-1)(\epsilon+2)\beta_T]/3 \quad (7)$$

where β_T is the isothermal compressibility. To check the validity of this approximation, $(\partial \epsilon / \partial p)_T$ was calculated for carbon disulphide and for benzene, using eqn (7) and published values of ϵ and β_T , and was then compared with $(\partial \epsilon / \partial p)_T$ obtained by direct measurement. The calculated value differed from the measured one by 3% for CS_2 ²⁸ and by 10% for benzene.²⁹ This accuracy is sufficient for the present purpose, having regard to the other approximations inherent in the Born model for solvation.

The isothermal compressibilities of the molten mercuric halides were recalculated from ultrasonic velocity data reported by Bockris *et al.*,³⁰ using the equations and constant pressure specific heats given in their paper, but taking densities and expansivities from ref. 6. The value of β_T for HgI_2 listed by Bockris appears to have been wrongly calculated from the experimental data. The term $(\partial r / \partial p)_T$ in eqn (6) could be estimated from compressibility measurements on the solid mercuric halides, but unfortunately none have been made. The values adopted were based on the compressibilities of solid TlCl , TlBr and TlI .³¹ As table 1 shows, the contribution to $\overline{\Delta V}^\circ$ from this term is relatively small, so the final value obtained for $\overline{\Delta V}^\circ$ is not strongly influenced by errors in $(\partial r / \partial p)_T$.

The Born equation refers to spherical ions of radius r . Neither HgX^+ nor HgX_3^- is spherical. Two methods of calculation were used:

Method 1. For each ion, the value of r used was that of a sphere having the same volume,

Method 2. For HgX^+ , the positive charge was taken to be at the centre of the Hg atom, and the solvent was assumed to be unpolarized over the solid angle subtended by the X atom at the Hg nucleus. For HgX_2^- , the X atoms were assumed to bear a charge $-e/3$, and each X atom did not polarize the solvent in the solid angle subtended by the rest of the molecule at the X nucleus.

To illustrate the relative importance of the terms in eqn (6), the contributions to $\overline{\Delta V}_2^\circ$, calculated by Method 2, are listed in table 1. The last term in eqn (5), $RT(\partial \ln f_{\pm}/\partial P)_T$, was evaluated by the use of the Debye-Hückel expression for the mean ion activity coefficient in a uni-univalent electrolyte solution³²

$$\ln f_{\pm} = -\frac{(4.15 \times 10^6)c^{\frac{1}{2}}}{(\epsilon T)^{\frac{3}{2}}}(c \text{ in mol dm}^{-3})$$

Differentiating with respect to P ,

$$RT\left(\frac{\partial \ln f_{\pm}}{\partial P}\right)_T = \frac{(4.15 \times 10^6)c^{\frac{1}{2}}}{2(\epsilon T)^{\frac{3}{2}}}\left[-RT\left(\frac{\partial \ln c}{\partial P}\right)_T + \frac{3RT}{\epsilon}\left(\frac{\partial \epsilon}{\partial P}\right)_T\right]$$

Again assuming that $-RT(\partial \ln c/\partial P)_T \approx \Delta V_{\kappa}$,

$$RT\left(\frac{\partial \ln f_{\pm}}{\partial P}\right)_T \approx \frac{(2.08 \times 10^6)c^{\frac{1}{2}}}{(\epsilon T)^{\frac{3}{2}}}\left[\Delta V_{\kappa} + \frac{3RT}{\epsilon}\left(\frac{\partial \epsilon}{\partial P}\right)_T\right] \quad (8)$$

Jander and Brodersen³³ made e.m.f. measurements using gold electrodes in solutions of NaBr in HgBr_2 , and deduced that the concentrations of HgBr^+ and HgBr_2^- in fused HgBr_2 at 250°C are $1.4 \times 10^{-4} \text{ mol dm}^{-3}$. Using this figure for c , and the values of ϵ and $(\partial \epsilon/\partial P)_T$ listed in table 1, we find that $RT(\partial \ln f_{\pm}/\partial P)_T = -4.6 \text{ ml mol}^{-1}$. The ion concentrations in fused HgCl_2 and HgI_2 are not known, but they can be estimated crudely from the value for HgBr_2 on the assumption that the conductivity is proportional to c for the three compounds. On this basis, $RT(\partial \ln f_{\pm}/\partial P)_T$ is found to be -2.4 ml mol^{-1} for HgCl_2 and -56 ml mol^{-1} for HgI_2 , at their respective melting points. This volume term is seen to be insignificant for HgCl_2 and HgBr_2 , but not for HgI_2 . Table 2 shows that the calculated value of $-\overline{\Delta V}^\circ$ for HgCl_2 and HgBr_2 is greater than $-2 \Delta V_{\kappa}$ by between 10 and 40 ml mol^{-1} , depending on the method of calculation, but for HgI_2 the calculated $-\overline{\Delta V}^\circ$ is 50 ml mol^{-1} less than $-2 \Delta V_{\kappa}$. The sign and magnitude of this difference between $\overline{\Delta V}_0$ and $2 \Delta V_{\kappa}$ for HgI_2 are such that it could reasonably be attributed to the term $2RT(\partial \ln f_{\pm}/\partial P)_T$ (cf. eqn (3)). A better estimate of this quantity cannot be made until the ion concentration in fused HgI_2 is measured experimentally. With this reservation, the agreement between the experimental $2 \Delta V_{\kappa}$ and the calculated $\overline{\Delta V}^\circ$ is as good as can be expected for the Born model, and provides support for the suggestion that the principal cause of the observed increase in conductivity with pressure is the displacement of the ionization equilibria $2\text{HgX}_2 \rightleftharpoons \text{HgX}^+ + \text{HgX}_2^-$ to the right with pressure. The volumes listed in table 1 show that the biggest contribution to $\overline{\Delta V}^\circ$ arises from the term $(Ne^2z^2/2r\epsilon^2)(\partial \epsilon/\partial P)$ of eqn (6). Substituting the expression for $(\partial \epsilon/\partial P)$ from eqn (7),

$$\overline{\Delta V}^\circ \approx -\sum (Ne^2z^2\beta_T/6r)(\epsilon-1)(\epsilon+2)/\epsilon^2 \quad (9)$$

The factor $(\epsilon-1)(\epsilon+2)/\epsilon^2$ is very close to unity for values of ϵ greater than 5. Since ϵ is between 5 and 10 for the mercuric halide melts, the calculated value of $\overline{\Delta V}^\circ$ is insensitive to errors in estimating ϵ . This is fortunate in view of the approximate method we were obliged to use. If eqn (5) and (6) are now combined, and the terms involving $(\partial r/\partial P)_T$ and $\ln f_{\pm}$ are omitted, the resulting expression for ΔV_{κ} is

$$\Delta V_{\kappa} \approx -\sum Ne^2z^2\beta_T/12r \quad (10)$$

This indicates that the largest pressure coefficients for conductivity in slightly ionized liquids are likely to arise when the ions produced are small and the liquid has high compressibility. Apart from the mercuric halides, these conditions are satisfied by the molten halides and oxyhalides of some of the elements in groups III, IV, V and VI of the periodic table, the interhalogen compounds and by liquid iodine itself, which is slightly ionized into I^+ and I_3^- .³⁶ Because the pressure coefficient of the ionization

TABLE 1.—VOLUME TERMS FOR THE SPECIES HgX_2 , HgX^+ AND HgX_3^- .

species	Hg—X bond length (10^{-10} m)	molecular volume (10^{-30} m ³)	temp. (°C)	ϵ	$10^4(\partial\epsilon/\partial P)$ (bar ⁻¹)	$10^6\gamma^{-1}(\partial\gamma/\partial P)$ (bar ⁻¹)	$(Ne^2/2r^2)\partial r/\partial P$ ($1-1/\epsilon$) (cm ³ mol ⁻¹)	$(Ne^2z^2/2re^2)\partial\epsilon/\partial P$ (cm ³ mol ⁻¹)
HgCl ₂	2.29 ^a	54.5	286	4.87	4.75	1.6	—	—
HgCl ⁺	2.2 ^c	31.2				1.6	6	87
HgCl ₃ ⁻	2.4 ^c	78.7				1.6	1	22
HgBr ₂	2.41 ^a	67.5	241	6.16	7.34	2.0	—	—
HgBr ⁺	2.3 ^c	37.6				2.0	7	81
HgBr ₃ ⁻	2.5 ^c	98.2				2.0	2	19
HgI ₂	2.59 ^a	88.5	257	9.52	20.8	2.3	—	—
HgI ⁺	2.5 ^c	48.0				2.3	8.5	95
HgI ₃ ⁻	2.70 ^b	129.5				2.3	2	21

^a ref. (34); ^b ref. (35); ^c estimated.

constant is expected to be large in these cases, there is a prospect that these compounds could be converted to completely ionized liquids by application of relatively modest pressures.⁴⁴ We estimate that the equilibria (1) would be displaced heavily to the right by pressures of the order 5-10 kbar only. This contrasts with the situation in water, for which $\Delta\bar{V}^\circ$ is only -20 ml mol⁻¹ and which requires pressures and temperatures

TABLE 2.—VOLUME TERMS FOR THE EQUILIBRIA $2HgX_2 \rightleftharpoons HgX^+ + HgX_3^-$

X	temp. (°C)	$\Delta\bar{V}^\circ$ (cm ³ mol ⁻¹)		$2\Delta V_\kappa$ (cm ³ mol ⁻¹)
		method 1	method 2	
Cl	286	-131	-116	-90
Br	241	-120	-109	-96
I	257	-132	-127	-178

in the region of 200 kbar and 1000°C for complete ionization.^{37, 38} These conditions have been reached only in shock waves, which severely restricts the range of experiments which can be carried out on the ionized liquid. For the liquids listed above, the pressures required for complete ionization are within the range of existing static techniques, and it should be possible to study in detail the variations in physical and chemical properties associated with the change from the molecular state at atmospheric pressure to the ionic state at high pressures.

TEMPERATURE DEPENDENCE OF ΔV_κ

Fig. 6 illustrates that ΔV_κ for HgI₂ and HgBr₂ varies linearly with temperature, becoming numerically greater as the temperature rises. This may be interpreted in terms of the approximate eqn (10), in which ΔV_κ and β_T are the only temperature-dependent quantities. Taking logarithms and differentiating,

$$\partial \ln(-\Delta V_\kappa)/\partial T = \partial \ln \beta_T/\partial T \quad (11)$$

i.e. the relative increase in $(-\Delta V_\kappa)$ with temperature should be equal to the relative

increase in isothermal compressibility if the theory leading up to eqn (10) is correct. Mean values of $\partial \ln(-\Delta V_{\kappa})/\partial T$ have been measured over a temperature range of 100 K for HgI_2 and HgBr_2 , and compared with $\partial \ln \beta_T/\partial T$ calculated from sound velocity data.³⁰ For HgBr_2 the change in sound velocity over the temperature range investigated was less than the experimental precision at any one temperature (5%), so the calculation is unreliable. For HgI_2 , a 10% change in sound velocity was recorded over a 70 K temperature interval. In this case, $\partial \ln(-\Delta V_{\kappa})/\partial T$ and $\partial \ln \beta_T/\partial T$ were respectively 3.3×10^{-3} and $2.7 \times 10^{-3} \text{ K}^{-1}$. With the reservation that the second quantity is subject to considerable experimental uncertainty, this agreement provides further support for the model and for the approximate eqn (10).

TEMPERATURE DEPENDENCE OF CONDUCTIVITY AT CONSTANT DENSITY

If X is any intensive property of a substance, which depends only on the pressure, volume and temperature, the isochoric and isobaric temperature derivatives of X are related by the standard expression

$$(\partial X/\partial T)_V = (\partial X/\partial T)_P + (\partial P/\partial T)_V (\partial X/\partial P)_T.$$

Writing $\ln \kappa$ for X , and defining $E_V = -R[\partial \ln \kappa/\partial(1/T)]_V$ and $E_P = -R[\partial \ln \kappa/\partial(1/T)]_P$, it follows that

$$\begin{aligned} E_V &= E_P - T(\partial P/\partial T)_V \Delta V_{\kappa} \\ &= E_P - (\alpha T/\beta_T) \Delta V_{\kappa} \end{aligned} \quad (12)$$

(α = expansivity). In the introduction we noted that E_P is negative for HgI_2 at atmospheric pressure, and for HgBr_2 and HgCl_2 E_P is positive at low temperatures but negative at higher temperatures. Fig. 6 shows that ΔV_{κ} is a large, negative volume, increasing numerically with increasing temperature. The energy term $-(\alpha T/\beta) \Delta V_{\kappa}$ is therefore positive, and is sufficiently large to make E_V positive for all three mercuric halides over the temperature range covered in our work. Table 3 shows values of E_P and E_V for the three halides, at various temperatures. These results confirm the suggestion made by Grantham and Yosim,¹ that the decrease in conductivity with rising temperature is due essentially to the density change. If the density is held constant, κ increases with temperature in the "normal" way. We infer that the observation of a negative value for E_P for a partly ionized liquid makes it likely that ΔV_{κ} will be large and negative, for only if this is so can E_V be positive. Apart from HgI_2 , negative E_P values have been reported¹ for molten InCl_3 , InBr_3 , I_2 ,³⁶ BrF_3 ³⁹⁻⁴¹ and, at higher temperatures,¹ for CuCl , ZnI_2 , CdI_2 , InI_3 and SnCl_2 . These compounds belong to the categories listed in a previous section, which confirms the conclusion that their degree of ionization is expected to increase steeply with pressure.

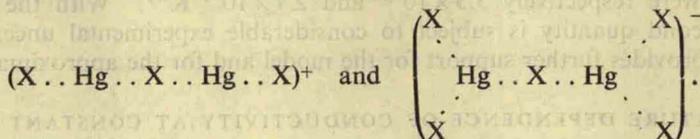
TABLE 3.—ISOBARIC AND ISOCHORIC ACTIVATION ENERGIES FOR CONDUCTIVITY IN FUSED MERCURIC HALIDES

halide	temp. (°C)	E_P (kJ mol ⁻¹)	E_V (kJ mol ⁻¹)
HgCl_2	286	25.7 ^a	57.3
HgBr_2	241	25.9 ^a	56.1
	315	19.2 ^a	64.4
	450	0.0 ^b	(73)
HgI_2	257	-10.5 ^c	35.7
	300	-13.0 ^c	37.7
	350	-14.7 ^c	39.7

^a ref. (6); ^b ref. (1); ^c calculated from data in ref. (7). The value in brackets is approximate. α , β and ΔV_{κ} at 450°C were found by extrapolation from lower temperatures.

POSSIBILITY OF CHARGE TRANSFER BY A GROTTIUS MECHANISM

Throughout the discussion it has been assumed that the mobilities of the ions in HgX_2 melts vary only slightly with pressure. This assumption is unexceptionable if conduction occurs by normal migration of the ions HgX^+ and HgX_3^- . However, conduction could also occur by transfer of X^- between either of these ions and an HgX_2 molecule, *via* transition states such as



We reconsider our assumption in the light of this possibility.

The total activation volume for these transfer processes (ΔV^\ddagger) is the sum of the volume change in the molecules themselves when the transition state is formed from the reactants (ΔV_1^\ddagger) and the change in solvent volume arising from charge redistribution (ΔV_2^\ddagger). Using methods outlined by Hamann,^{4,2} and assuming that the $\text{Hg} \cdots \text{X}$ bonds in the halogen bridge of the transition state are 10 % longer than those in the molecule which the X atom is leaving, we estimate that ΔV_1^\ddagger is about -3 ml mol^{-1} and -2 ml mol^{-1} for the two structures shown above, respectively. ΔV_2^\ddagger is more difficult to estimate, because it requires a knowledge of the charge distribution in the reactants and the transition state. If it is assumed that the charge is evenly distributed over the atoms in the transition state, and if method 1 (above) is used to calculate the change in solvent electrostriction when the transition state is formed, ΔV_2^\ddagger is found to be $+22 \text{ ml mol}^{-1}$ for I^- transfer between HgI_2 and HgI^+ , and $+9 \text{ ml mol}^{-1}$ for transfer between HgI_3^- and HgI_2 . These positive volumes arise because the transition states are larger than the respective reactant ions HgI^+ and HgI_3^- , resulting in a release of solvent when the transition state is formed. However, this volume increase would be partly offset if a negative charge developed on the bridging X atom in the saddle point configuration. There is evidence that a similar effect occurs in isotope exchange reactions of the type $\text{X}^{*-} + \text{RX} \rightarrow \text{RX}^* + \text{X}^-$, which resemble the reactions discussed here; entropy of activation measurements suggest that the group R acquires a positive charge as it reaches the saddle point.^{4,3} In these reactions the experimental ΔV^\ddagger could be accounted for on the basis of ΔV_1^\ddagger alone; ΔV_2^\ddagger was approximately zero because of cancellation of the contributions from the two effects just mentioned. This consideration, together with the small magnitude of the above estimates for ΔV_1^\ddagger and ΔV_2^\ddagger compared with $\overline{\Delta V}^\circ$ for self-ionization, make it unlikely that changes in mobility with pressure make a significant contribution to the observed increase in conductivity with pressure, even if a Grotthus mechanism operates.

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