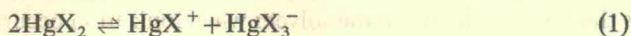
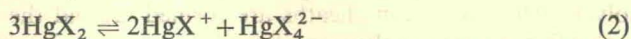


## EFFECT OF PRESSURE ON THE DEGREE OF IONIZATION

Comparison of vapour-phase and liquid-phase Raman spectra shows that, at atmospheric pressure, the fused mercuric halides consist predominantly of linear molecules  $\text{HgX}_2$ .<sup>6, 10-13</sup> The conductivity has been attributed<sup>1, 6</sup> to slight self-ionization with formation of complex ions



and, to a lesser extent,



The ions  $\text{HgX}^+$ ,  $\text{HgX}_3^-$  and  $\text{HgX}_4^{2-}$  cannot be detected in the pure melts by Raman spectroscopy, but  $\text{HgX}^+$  has been found in aqueous solutions of  $\text{HgX}_2$  with added  $\text{Hg}(\text{ClO}_4)_2$ ,<sup>14</sup> and spectra due to  $\text{HgX}_3^-$ , and ultimately  $\text{HgX}_4^{2-}$ , appear when alkali metal halides are added to molten  $\text{HgX}_2$ .<sup>15, 16</sup> Band intensity data<sup>15</sup> indicate that equilibrium (2) may be ignored in pure  $\text{HgX}_2$  melts at atmospheric pressure.

Previous work on fully ionized melts, such as the alkali metal nitrates<sup>2</sup> or halides,<sup>17</sup> 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.<sup>18-21</sup> 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 Grotthuss mechanism, e.g. for proton transfer.<sup>5</sup> 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.<sup>22, 23</sup> The same consideration applies to the self-ionization of molecular liquids such as water.<sup>24</sup> 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  $\text{HgX}^+$  and  $\text{HgX}_3^-$ . 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  $\text{HgX}^+$  and  $\text{HgX}_3^-$  minus the volume of two  $\text{HgX}_2$  molecules, and has been calculated from the appropriate bond lengths and van der Waals radii. The ions  $\text{HgX}_3^-$  were taken to be planar and trigonal. The van der Waals radii used were <sup>25</sup> (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  $1 \text{ ml mol}^{-1}$  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  $\text{HgX}_2$ .  $\overline{\Delta V}_2^\circ$  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  $\epsilon$  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 <sup>26</sup>

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

The terms in the square bracket can be evaluated if  $\epsilon$ ,  $r$  and their pressure derivatives are known. For the mercuric halides, experimental values of  $\epsilon$  are available only for the solids.<sup>27</sup> Since the crystals contain non-polar molecules  $\text{HgX}_2$  (in the case of  $\text{HgI}_2$ , this applies to the yellow modification),  $\epsilon$  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.<sup>6</sup> 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  $\beta_T$  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  $\epsilon$  and  $\beta_T$ , 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  $\text{CS}_2$ <sup>28</sup> and by 10 % for benzene.<sup>29</sup> 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.*,<sup>30</sup> using the equations and constant pressure specific heats given in their paper, but taking densities and expansivities from ref. 6. The value of  $\beta_T$  for  $\text{HgI}_2$  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  $\text{TlCl}$ ,  $\text{TlBr}$  and  $\text{TlI}$ .<sup>31</sup> 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  $\text{HgX}^+$  nor  $\text{HgX}_3^-$  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,