

**Method 2.** For  $\text{HgX}^+$ , 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  $\text{HgX}_3^-$ , 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  $\overline{\Delta V}^\circ$ , 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 solution<sup>32</sup>

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

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 Brodersen<sup>33</sup> made e.m.f. measurements using gold electrodes in solutions of NaBr in  $\text{HgBr}_2$ , and deduced that the concentrations of  $\text{HgBr}^+$  and  $\text{HgBr}_3^-$  in fused  $\text{HgBr}_2$  at  $250^\circ\text{C}$  are  $1.4 \times 10^{-4} \text{ mol dm}^{-3}$ . Using this figure for  $c$ , and the values of  $\epsilon$  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  $\text{HgCl}_2$  and  $\text{HgI}_2$  are not known, but they can be estimated crudely from the value for  $\text{HgBr}_2$  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  $-2.4 \text{ ml mol}^{-1}$  for  $\text{HgCl}_2$  and  $-56 \text{ ml mol}^{-1}$  for  $\text{HgI}_2$ , at their respective melting points. This volume term is seen to be insignificant for  $\text{HgCl}_2$  and  $\text{HgBr}_2$ , but not for  $\text{HgI}_2$ . Table 2 shows that the calculated value of  $-\overline{\Delta V}^\circ$  for  $\text{HgCl}_2$  and  $\text{HgBr}_2$  is greater than  $-2 \Delta V_\kappa$  by between 10 and  $40 \text{ ml mol}^{-1}$ , depending on the method of calculation, but for  $\text{HgI}_2$  the calculated  $-\overline{\Delta V}^\circ$  is  $50 \text{ ml mol}^{-1}$  less than  $-2 \Delta V_\kappa$ . The sign and magnitude of this difference between  $\overline{\Delta V}^\circ$  and  $2 \Delta V_\kappa$  for  $\text{HgI}_2$  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  $\text{HgI}_2$  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  $2\text{HgX}_2 \rightleftharpoons \text{HgX}^+ + \text{HgX}_3^-$  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  $(Ne^2 z^2 / 2r\epsilon^2)(\partial \epsilon / \partial P)$  of eqn (6). Substituting the expression for  $(\partial \epsilon / \partial P)$  from eqn (7),

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

The factor  $(\epsilon - 1)(\epsilon + 2)/\epsilon^2$  is very close to unity for values of  $\epsilon$  greater than 5. Since  $\epsilon$  is between 5 and 10 for the mercuric halide melts, the calculated value of  $\overline{\Delta V}^\circ$  is insensitive to errors in estimating  $\epsilon$ . 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  $\Delta V_\kappa$  is

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

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  $I_3^-$ .<sup>36</sup> Because the pressure coefficient of the ionization

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

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

<sup>a</sup> ref. (34); <sup>b</sup> ref. (35); <sup>c</sup> 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.<sup>44</sup> 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<sup>-1</sup> and which requires pressures and temperatures

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

| X  | temp.<br>(°C) | $\Delta \bar{V}^\circ$<br>(cm <sup>3</sup> mol <sup>-1</sup> ) | $2\Delta V_K$<br>(cm <sup>3</sup> mol <sup>-1</sup> ) |      |
|----|---------------|----------------------------------------------------------------|-------------------------------------------------------|------|
|    |               | 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.<sup>37, 38</sup> 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 $\Delta V_K$

Fig. 6 illustrates that  $\Delta V_K$  for HgI<sub>2</sub> and HgBr<sub>2</sub> varies linearly with temperature, becoming numerically greater as the temperature rises. This may be interpreted in terms of the approximate eqn (10), in which  $\Delta V_K$  and  $\beta_T$  are the only temperature-dependent quantities. Taking logarithms and differentiating,

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

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