

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.

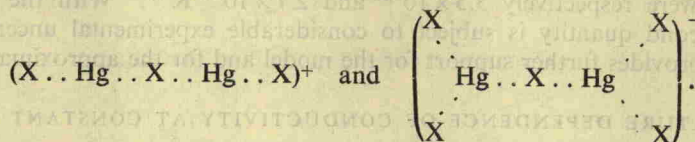
TABLE 3.—ISOBARIC AND ISOCHORIC ACTIVATION ENERGIES FOR CONDUCTIVITY IN FUSED MERCURIC HALIDES

halide	temp. (°C)	E_P (kJ mol ⁻¹)	E_V (kJ mol ⁻¹)
HgCl_2	286	25.7 ^a	57.3
	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 ($\Delta V^\ddagger$) is the sum of the volume change in the molecules themselves when the transition state is formed from the reactants ($\Delta V_1^\ddagger$) and the change in solvent volume arising from charge redistribution ($\Delta V_2^\ddagger$). Using methods outlined by Hamann,⁴² 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 $\Delta V_1^\ddagger$ is about -3 ml mol^{-1} and -2 ml mol^{-1} for the two structures shown above, respectively. $\Delta V_2^\ddagger$ 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, $\Delta V_2^\ddagger$ 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.⁴³ In these reactions the experimental $\Delta V^\ddagger$ could be accounted for on the basis of $\Delta V_1^\ddagger$ alone; $\Delta V_2^\ddagger$ 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 $\Delta V_1^\ddagger$ and $\Delta V_2^\ddagger$ 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 Grotthuss mechanism operates.

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