B. CLEAVER AND S. I. SMEDLEY

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 HgI₂ and HgBr₂, and compared with $\partial \ln \beta_T/\partial T$ calculated from sound velocity data.³⁰ For HgBr₂ 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 HgI₂, 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 2.7×10^{-3} 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

$$E_{V} = E_{P} - T(\partial P/\partial T)_{V} \Delta V_{\kappa}$$

$$= E_{P} - (\alpha T/\beta_{T}) \Delta V_{\kappa}$$
(12)

(α = expansivity). In the introduction we noted that E_P is negative for HgI₂ at atmospheric pressure, and for HgBr2 and HgCl2 Ep 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 $-(\alpha T/\beta)$ ΔV_{κ} 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, k 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 HgI₂, negative E_P values have been reported ¹ for molten InCl₃, InBr₃, I₂, ³⁶ BrF₃ ³⁹⁻⁴¹ and, at higher temperatures,1 for CuCl, ZnI2, CdI2, InI3 and SnCl2. 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

	temp.	Ep	E_V
halide	(°C)	(kJ mol-1)	(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.

CONDUCTIVITY OF FUSED MERCURIC HALIDES

POSSIBILITY OF CHARGE TRANSFER BY A GROTTHUS 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

ito considerable experimental unera	X	15
$(X \dots Hg \dots X \dots Hg \dots X)^+$ and	HgXHg	
בסאסובדועודע הי בסאגדאאד ב	X ¹ DEPENDENCE X)

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 $(\Delta V_{\tau}^{\dagger})$ and the change in solvent volume arising from charge redistribution (ΔV_2^{\ddagger}). Using methods outlined by Hamann,⁴² and assuming that the Hg. . 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}^{\dagger} 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_{3}^{\ddagger} is found to be $+22 \text{ ml mol}^{-1}$ for I⁻ transfer between HgI₂ 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 $X^{*-} + RX \rightarrow RX^{*} + X^{-}$, 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 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 $\Delta V_{\pm}^{\ddagger}$ and ΔV_{\pm}^{\pm} compared with ΔV° 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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